Science and Technology of Polymers
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Lecture – 30
Environmental Degradation of Polymers

Today, as we discuss about the degradation of polymers, polymer products which actually (( )) exposed to the environment. Now, polymers or polymer products are basically organic materials, made of carbon, hydrogen, nitrogen, oxygen, sulphur etcetera. Basically, if you see there are two categories of polymers and its purely hydrocarbon polymers, and the others are polymers containing heteratoms like oxygen, nitrogen, sulphur included in the polymer structure. So, the degradation and stability of those different polymer products containing such polymers of hydrocarbon category or category containing oxygen, nitrogen, sulphur, along with carbon hydrogen.

In the environment there are agencies like oxygen, heat, electromagnetic radiation, ozone, these cause the polymers to the degraded by their influence. So, when polymer products are in use, they get exposed to such agencies and they need to be stabilized with some additives or ingredients. Otherwise polymers will continue to degrade and the long term properties of the polymer products will gradually decrease. So, before going to manufacture any polymer product, we must know the degradation and stabilisation of stability aspects of those polymer products, containing the basic polymer materials inside the product.

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The process of degradation and the mechanism of degradation and in which agencies, in the presence of which agencies these polymers degrades most or remains more stable, that is the subject matter of this lecture. Now, environment degradation of polymers they mean, that when polymer products are exposed to the environment, then environment there is humidity which vary from 30 to 95 percent and sunlight, oxygen, ozone, thermal effects for other electromagnetic radiations, that cause the degradation, chemical degradation.

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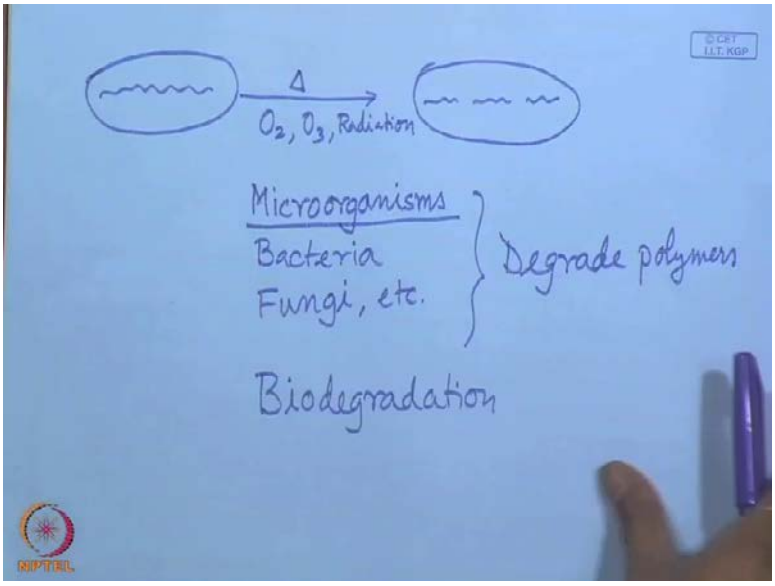

The degradation, I mean a polymer say having this kind of molecular configuration, this environment agencies contains thermal influence or oxygen, ozone, radiation etcetera. This degrades the polymers into sort of fragrance and molecular size of the polymers as a whole is reduced. Naturally, the properties of these polymers will be affected, that means properties have been with this the polymer molecules have been full molecular length molecular length will not be available after it is degraded. That means product is destroyed, into the degradation of the polymer chain. Apart from this effect of oxygen, ozone, heat from the environment, there can be agencies like micro organisms. These micro organisms may be bacteria, fungi etcetera, which attack the carbonations materials this polymers and degrades the polymers.

During such degradation of polymers by the influence of by the action of micro organisms, they produces carbon dioxide and some bio mass and some amount of carbon is been utilised as their food, from this polymers by the micro organisms. So, that kind of degradation by micro organisms in biological environment etcetera or biological influence, we can call that as biodegradation. Other than bio degradation, we can say the degradation of polymers can be due to oxygen, ozone and radiation effects, heat effects of the thermal influence etcetera. So, they degrades also there to smaller fragments and to some extent they degrades into carbon dioxide, where in the extreme situation carbon dioxide and water, extreme situation.

They degrade and form these products. Now, what is the necessary of this biodegradation or thermal degradation in there, any necessity? Now, the thermal degradation means or thermal degradation or degradation due to effects of oxygen, ozone, radiation, that occurs very slowly due to the environmental effect and chemical degradation, what is called chemical degradation? Biodegradation, if the products are exposed to micro organisms biological environment, that polymers are degrade it and that it gradually changes from the time when they are manufacture. Now, today there is need of this biodegradation, why there is a need of biodegradation?

Now, polymers being hydrocarbon in nature, carbonations materials like containing or other than carbon, hydrogen, oxygen nitrogen hetero atoms are present these polymers are not degraded at very faster rate. So, when some products made out of polymers are used by humans what happens? After the completion of the service of those products these products need to be disposed. If such products are disposed to the environment what happens? It gets

piled up at differed corners at different corners at different places at roadsides, the dumping ground and cause of lot of nuisance and that is called environmental nuisance or environmental pollution.

So, if such plastic polymeric wastes are generated, by the image of such polymeric products, there must be some suitable waste management mechanism or system, so that we can prevent such environmental nuisance or pollution, due to the littering of that polymer wastes. There are some techniques of waste management, the one is land filing, such polymers can be used for is as a land filled material or such waste can be incinerated, so that it will vanish due to combustion and we can get rid of piling of plastic wastes. But that is, there is also for incineration products. After incineration that generates carbon dioxide and carbon monoxide and other toxic hazardous gas, which pollutes in the air environment, that is not desirable.

Another thing is mechanical degradation, such product can be mechanical degraded and mixed up with or it can be again same for land filling. The last one is, last option is biodegradation. That means it the nature itself can take care of such plastic wastes of due to the creation of such plastic materials. Then, this problem can be solved in a better way. That means if the micro organisms can eat can consume such material as their food, then it will be slowly observed by the nature as is done in (( )) are the natural occurring material like wood and or other carbonations materials from plant and animal sources, which is created by nature. So, that is a very good approach which is the need of the day, today that people are thinking of producing biodegradable polymers rather than producing non biodegradable polymers.

Today people are thinking of green technology concept and under this green technology concept people are trying to synthesize or modify residue occuring polymers, which will be degraded by micro organisms. Now, what are the polymer types that need to be degraded, say first it is a commodity polymer items, in the form of films and moulded items. After their use they through it to the dustbin or garbage, these are the nature of the polymer items, which need to be degraded. Other kind of things are say biomedical implant items made of polymers. For example, disposable syringe (( )) system or surgical cloves or other biomedical implant material made of polymers, these things need to be degraded by micro organisms.

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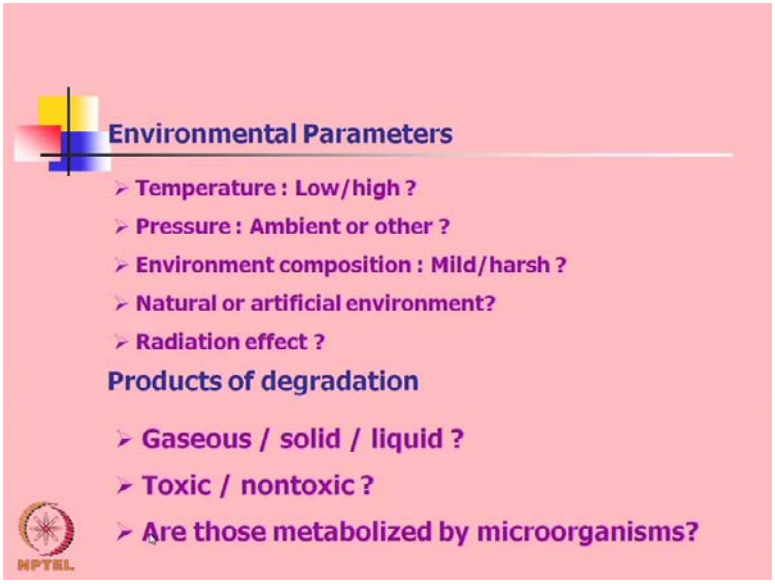

Now for such degradation what environmental parameters, we should consider for such micro (( )) degradation. Now, temperature is a first one most important parameter, at what temperature these polymers will be great? Is it the low or is it very high? What is the requirement? Now there are certain regions that high altitude, where our soldiers are fighting and for their some food materials and other things carried over there with some plastic packaging films. Now, in those areas, such polymers gets packaging films, polymers piled up because the temperature is subzero at subzero temperature dose not degrade because micro organisms cannot function at that very low temperature. Very high temperature once again, that is also we cannot think of degradation by micro organisms, were micro organisms cannot sustain.

But at very high temperature if we want degrade the polymers, that is a kind of incineration, so that is different thing, but we have to think of a temperature range within the ambient range of temperature, so that such polymer can be degraded by micro organisms. Pressures or what pressure or other, we must think. Environmental composition, is it very mild or harsh? That means, what are the agencies present in the environment, like harsh environment like ozone error things or high energy electromagnetic degradation like that, then natural or artificial environment or radiation effect. Products of degradation that can be gaseous product, solid product or liquid product; it can be toxic or nontoxic. And we have to think, whether such product could be metabolized by micro organisms or not? We have to think then we must find out a suitable means by which polymers can be degraded.

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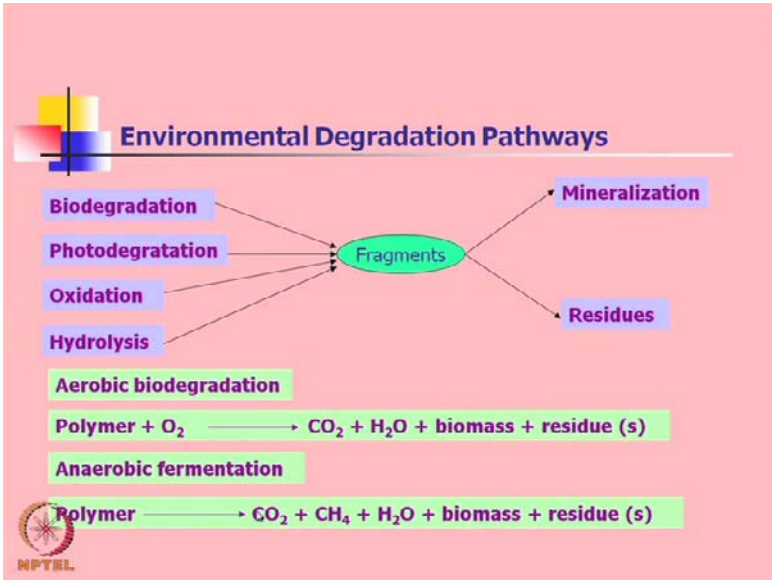

Now, if we think of the parts by which the polymers can be degraded by environmental means. Say we can think of biodegradation by the influence of micro organisms or photo degradation through electromagnetic degradation or oxidation by incorporating, by mixing some oxidizing agents or reacting with some oxidants, these polymers can be degraded or polymers can be hydrolytically degraded or you can say chemically degraded, say by the presence of acids and alkali these polymers cannot to be degraded. After degradation by these agencies the polymers will be broken into smaller pieces, called fragments of such low molecular wastes.

Now, such low molecular wastes fragments can be mineralised or they remain on the art as it is residues. In case of biodegradation, there can be of two types of biodegradation, one is aerobic biodegradation and the other is anaerobic degradation or we can say fermentation etcetera. Now, polymer in presence of oxygen is converted to carbon dioxide water, biomass and residue. Similarly, in case of anaerobic degradation, apart from carbon dioxide water some hydrocarbon gasses methane produced and biomass and residue will also be produced.

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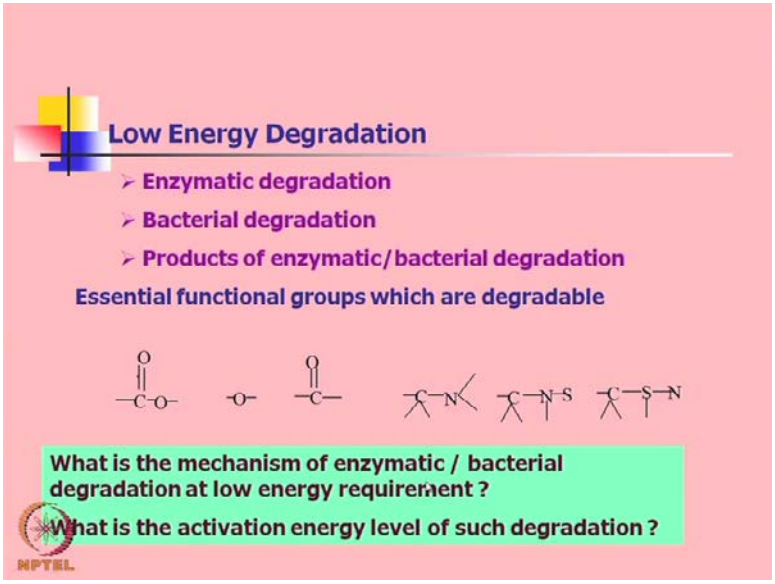

Now a positive would be suitable, if it is low energy process, energy involvement is very low, in that case we can think of degradation by enzymes, we can think of degradation by bacteria or fungi etcetera or next we have to think, what are the products of enzymatic and bacterial degradation, what happens during micro (( )) degradation? Microbes approach the surfaces of such plastic products and they will sit on the surface of those polymeric products, provided the suitable surface energy of those plastic products is suitable to them otherwise, those plastics cannot do not allow the microbes, unable to sit on the plastic seeds.

Now, if there is favourable environment like favourable energy, surface energy, then microbes can sit on the plastic surface polymer surface. Then they slowly try to get some nutrients from the substrate surface and they metabolise the polymer and produce some enzymes and produce some metabolic product. This way they create a bio film over the surface, then slowly they increase the population, their population and microbial colony will be formed on the surface at different regions.

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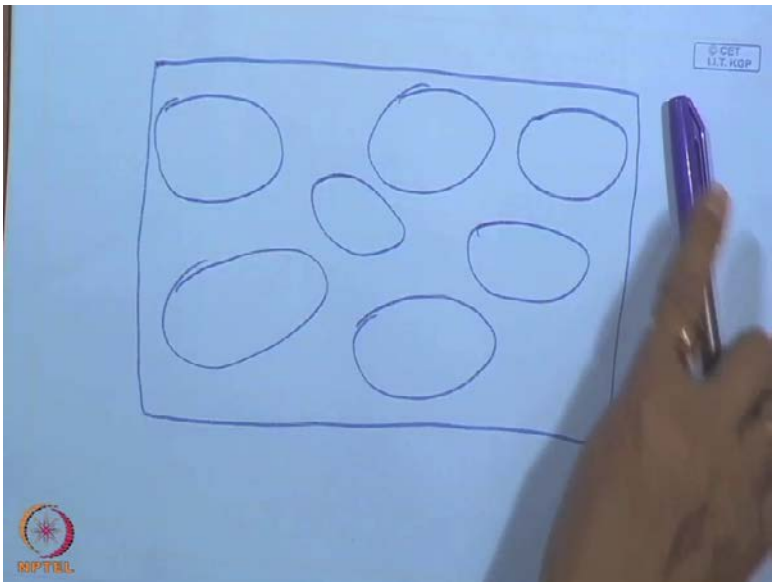

In those microbial colonies polymers will be eaten or be converted to some other smaller fragments, simpler products and the microbes will consume these polymers to get their carbon source as metabolic products will form some bio film. This show a slowly they will degrade the polymer surface and the polymer if it is polynomial film, that film will be week and it will be fragment in to smaller pieces.

Now, we must think of what will be the kind of polymers? What will be the nature of polymers, their structure and their configuration, which would be degraded by micro organisms. From the scientific point of view we must think of what are the functional groups which are present in polymer, so that those function groups the presents of the function group make the favourable situation for micro organisms to form their colonies on their surface. So, these are extra functional groups like this, extra functional group, their functional group, cationic functional group, hydroxyl group like this

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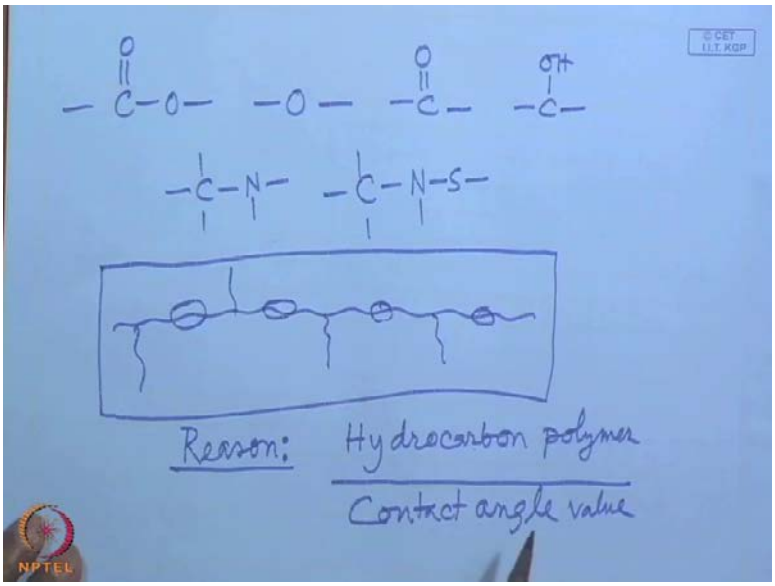

Polymer containing carbon, nitrogen, zinc and like this in differ form. Polymers containing carbon, nitrogen along with sulphur like this. Now, if such groups are present along the back bone chain of the polymer some regions like this or they remain as a pentane groups, in the polymer. Both can possible and both are there in different commercial plastic products. Such polymers will be a favourable for degradation by micro organisms. What is the reason for such? Reason is, if we think of hydrocarbon fume or, hydrocarbon polymer, surface energy of such polymer products of such energy of such polymer products are very high. That can be understood by contact angle value of that polymer surface.

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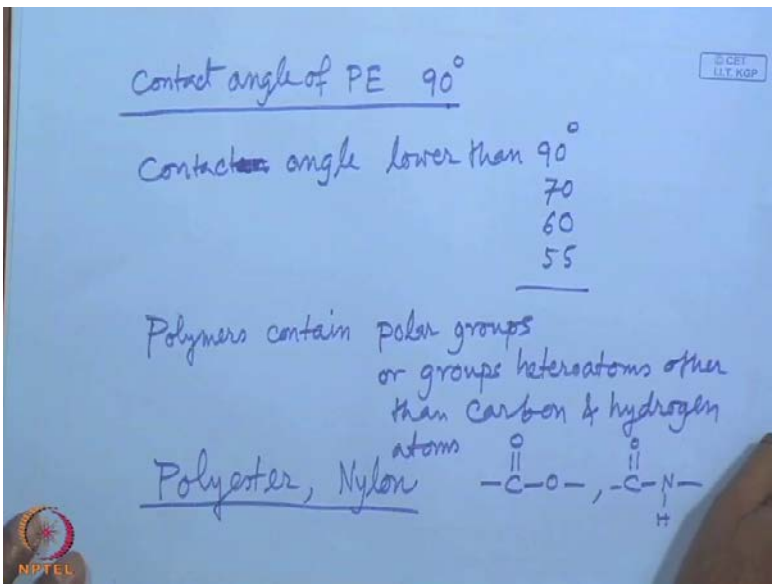

It is been found that contact angle of poly ethylene is a 90 degree. Now such contact angle of poly ethylene surface having such contact angle is not suitable for micro degradation. Now, if the contact angle is hallow, if the contact angle hallow is lower than 90 degree, say may be 70 degree or it may be 60 degree, may be 55 degree even less than that, that is more favourable such contact angle values of surfaces are more favourable micro organisms to see it over there.

That occurs when polymer contain such polar groups or groups containing hetero atoms, other than carbon and hydrogen atoms. For example polyester, nylon, such polymers contain ester group and ester function groups, along the back bone of chain or this amide group along the backbone chain. Carbon hydrates, those polymers are polar type of polymers are the oxygen atoms attach to the polymer chain, that makes the polymer degradable by micro organisms because such polymers this over surface energy becomes favourable for them. We must think of what is the mechanism of enzymatic degradation at low energy requirement, which will be a kind of efficient process. What is the activation energy level of such of degradation, we must analyse, we must calculate.

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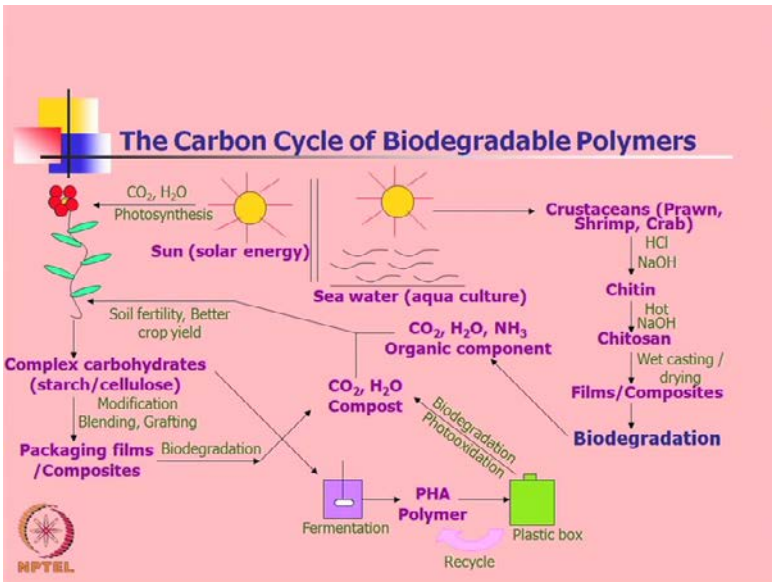

Now, let us look into the carbon cycle of biodegradable polymers. Here you see, in case of say plant system and plant kingdom, the plant bodies are found in the nature, synthesised in the nature by photo synthesis process through the observation of solar energy, in presence of carbon dioxide and water. So, plant bodies formed, this plant bodies contain

carbohydrates, proteins, liquids etcetera. Form complex carbohydrates, say example wood. Now, wood is a naturally occurring composite made of cellulose and lignin This cellulose and lignin in this polymers, both are polymers, cellulose is the reinforcing fibre and lignin is the matrix material continues phase material. Both these two matrix and reinforcing contains are our need of carbon, hydrogen and oxygen.

So, we can say these materials are carbon hydrates. Now, after such carbon hydrates plant materials of carbon hydrate are nature are available, we can modify those carbon hydrate materials. We can blend those with those other synthetic materials polymers. We can chemically modified through drafting of other chemical compounds, monomers onto the carbohydrates and we get new materials, which can be used for making products in the form of films, for use in the packaging industries, or we can make composites. Now, being carbohydrate nature, these polymers are degradable micro organisms say by bio degradation. Through by bio degradation of such naturally occurring materials that will produce carbon dioxide and water and compost.

These carbon dioxide and water and compost can increase the soil fertility, again that can help land growth and that will increase the crop yield. In other way such complex carbohydrates can be degraded by fermentation industries and fermentation process to produce a different kind of material known as poly hydroxide alkanoids polymers etcetera. Then, after use that can be thrown to the plastic box as garbage, after that again being this materials being are made of carbon, hydrogen, oxygen. They are degradable by micro organisms and bio degradation or they can also be degraded by sun light by reaction of ultraviolet component of sun light water and that will also produce carbon, hydrogen, oxygen and sum compost materials.

In other way if we think of the marine environment or in echo culture, different marine organisms are produced those marine organisms, we use for our suitable purpose. Now, we can take some few examples can be taken for the practice one say crustaceans, prawns, shrimps, crab etcetera. Now, we dispose this saves of such crustaceans, now those of saves of such crustaceans contain a value added material. If that can be harvested from crustaceans sales, we can make we can get polymer, like chitin or chitosan, a chemical treatment.

Basically of this chitosan is the acetilated form of chitin and this chitosan can be used as good material for making biodegradable films, we can make composites, we can (( )) or we can make value added products or we can make bio medical application. After use, that can be that will be produced as waste and that waste can be degraded by micro organ agents, producing this gaseous like carbon dioxide and ammonia. These are all organic components and this way we see, that a cycle is complete from if we see through the plant kingdom and animal kingdom, this way is fine ultimately these products are converted into carbon dioxide, water and compost trough the action of micro organisms.

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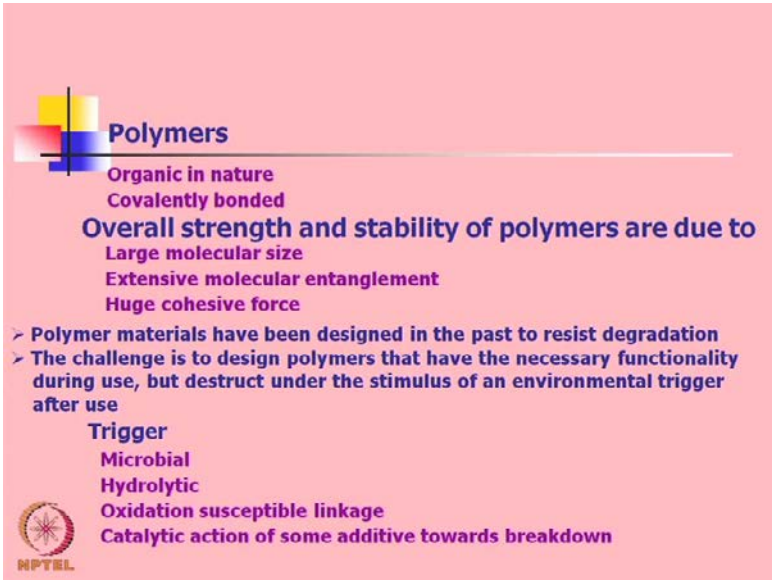

Now, this polymers are organic in nature. This polymers are covalently bonded, primary covalent bonds are there. In the product form apart from such covalent bonds, primary covalent bonds, there are huge secondary emerald bonds, which makes such polymers and very strong and tough. Overall strength and stability of polymers are due to the large molecular size. That means very high molecular weight of such polymer molecules. There is extensive and very huge entanglement of molecules. We can say inter molecular as well as intra molecular entanglement and huge cohesive force erasing out of secondary balance interaction forces.

All these three different categories of parameters, they make such polymers as very strong and very stable polymers in an environment. Now, after say 1970 polymer materials were designed to resist degradation. That means people wanted to make polymers stable as a

maximum stability of polymers. We wanted to develop maximum stability, that means polymers should be a high temperature, should not be degraded by environmental agencies like oxygen, heat and ozone etcetera are electromagnetic radiation. But people started realizing after seventies in a last century, that if these polymers do not degrade in some waste generated, there is no place keep such waste material and degraded material, otherwise it will be a nuisance to the environment.

So, people took this problem, challenge to design new polymers, which will be very strong and tough, durable during service, but after that use is over, they can be dispose them into environment and environment will take care by itself degradation, without causing any harm to the environment. Now, these are the microbial effect, microbial agencies, hydrolytic environment, oxidative environment, that presence of catalyst etcetera, so these can be used as trigger for degradation of the polymer materials.

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Now, while we approach to degrade the materials, polymer materials in the environment, we must think of the degradation products, so that the degradation product should not be toxic. That means you have to make the degradation process in such a way, so that the known products are produced in nature can take care of the further consumption. Such degradation product should be hazardous, not toxic degradation products should not pass to the environment and should not become completely utilized by soil micro organisms. Now,

bio degrade polymers, they are, there is a huge demand of, today and there is a huge demand of polymers.

They needs a market like a fast food vapours. We know today if go into the shop or purchasing any food items and any snacks or even milk or oil, we find those are packed in plastic films, plastic films are laminated by thin films. So, we find there is a need of polymers for packaging application, packaging are not by degradable, then that is a used problem. So, that need can be fulfil, if so packaging materials are produced by bio degradable polymers and made by bio degradable polymers. Say, it as like fast food wrappers agricultural films or mulches personal products marine and fresh water application etcetera and for compost banks etcetera. These are the areas where bio degradable polymers can sub there functions. Environmental disposal conditions for biodegradability or composting, soil marine environment, in wastewater treatment facility and anaerobic digesters.

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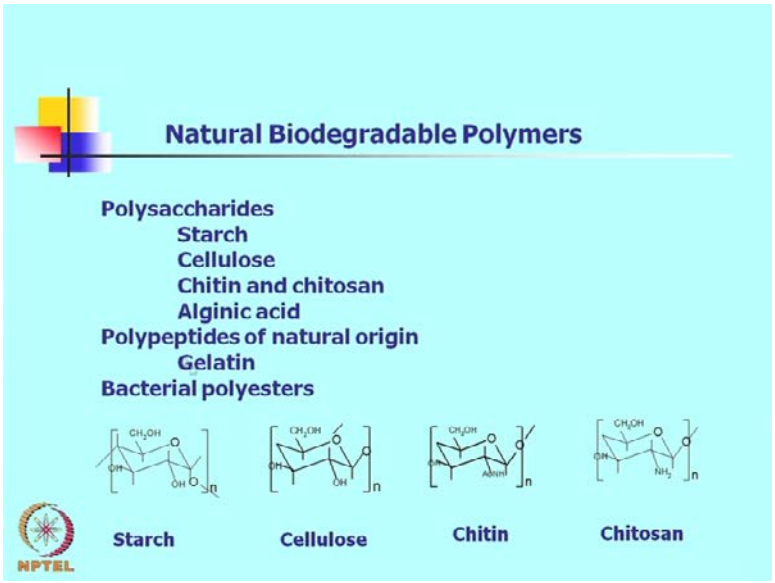

Let us look into the examples of bio degradable polymers. Say in the category of polysaccharides, we finds polymer starch cellulose chitin and chitosan, and agonic acid as well as the derivatives of chemical derivatives polymers or chemically modified polymers from this hydro materials. This could be good biodegradable polymers from such products can be made. Polypeptides of natural origin say gelatine, which is a natural protein gelatine

a bacteria also produces polymers known bacterial polyesters, say poly hydroxyl butyrate or poly hydroxyl.

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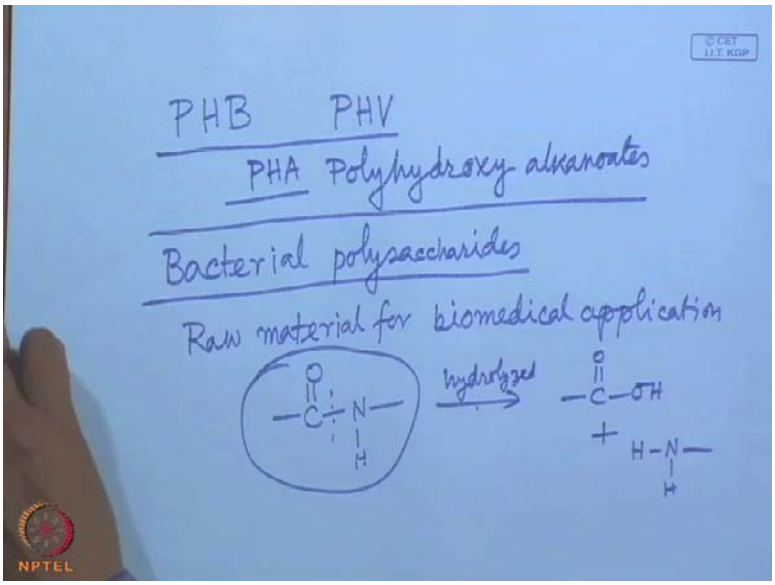

I will convert this butyrate in general polymers or poly hydroxyl will converts poly hydroxyl. Now, these polymers are produced by bacteria, these are called bacterial poly saccharine. These polymers bacterial polysaccharides are made or prepared for culture condition and this bacterial polysaccharides are very good raw materials for bio medical applications.

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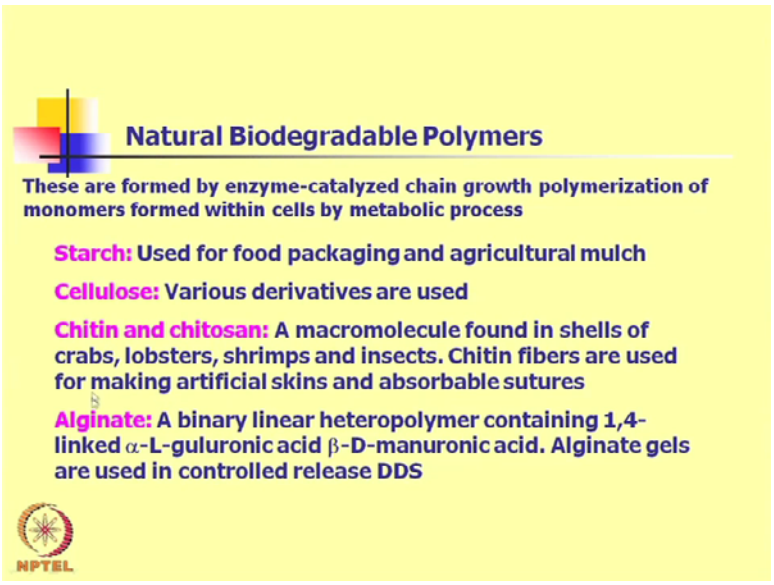

Now, these bio medical applications are these polymers, say starch, cellulose, chitin and chitosan or alginate bacteria polysaccharides. Particularly these bacteria, polysaccharides are formed by enzyme catalyzed chain growth polymerization of monomers, formed within cells by metabolic process. Starch, is used for food packaging and agricultural mulch, cellulose is used to various derivation are used for making a polymer slides like say cellulose acetate and cellulose butyrate chitin and chitosans. As told a macromolecule, these are macromolecule found in shells of crabs, lobsters, shrimps and insects. Chitin fibres are used for making artificial skins and absorbable sutures. Alginate are a class of polymer is a binary, linear, hetero polymer containing, 1 4 linked alpha L guluronic acid or beta D manuronic acid. Alginate gels are used in controlled release drug delivery system.

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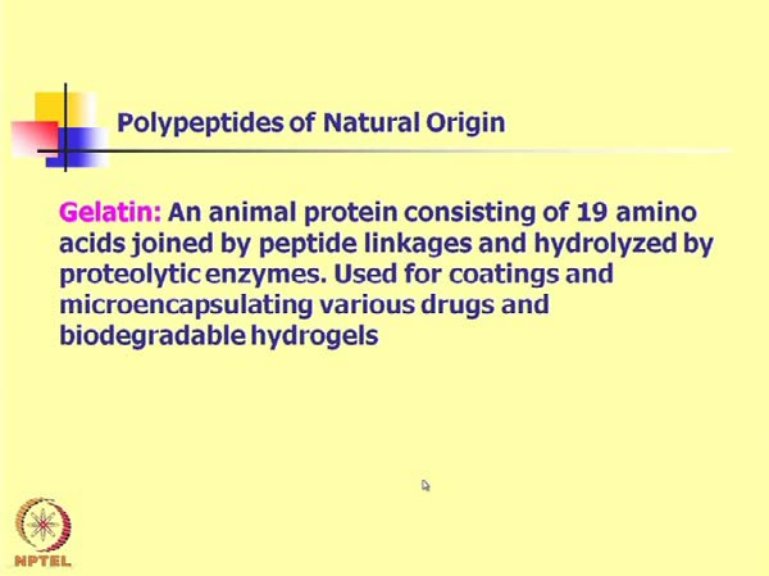

About gelatine, gelatine is the animal protein consisting of 19 amino acids joined by peptide linkages a peptide linkages are peptide linkages these are peptide linkage are, this is peptide linkages and these peptide linkages can be hydrolyzed. At this point it will break it will form acid amino derivative, acid derivative or amino derivative we can say. So, such polymers gelatines can degraded and hydrolyses using proteolyses enzymes, used for coating. Such polymers are used from gelatine polymers used for coating and microencapsulating various drugs and biodegradable hydro gels. This gelatine can also used for making composite along with other polymers.

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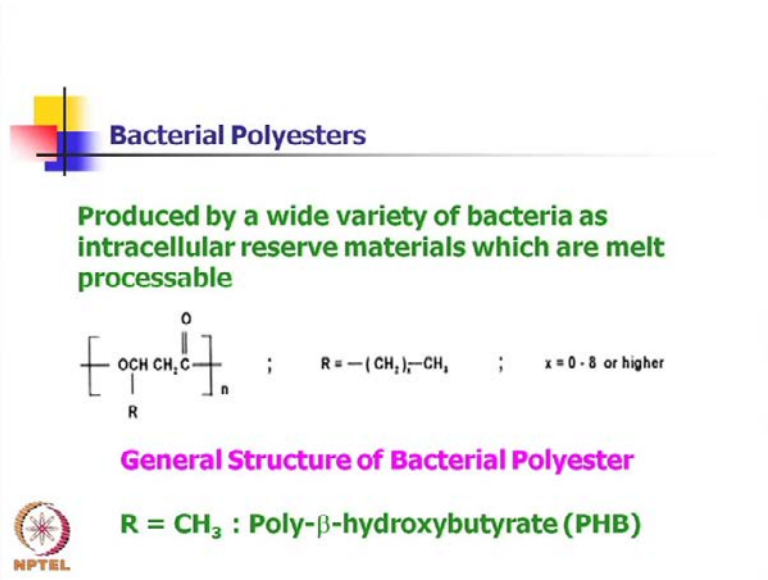

These are highly hydrophilic polymers and gelatines are highly hydrophilic polymers. Now, this bacterial polyesters, they produced by a wide variety of bacteria as intracellular reserve materials, which are melt processable. Now, this is a kind of, this is the general structure of bacterial poly or R group can be vary in hydrocarbon chain and x can be 0 to 8 or higher. Now, this R can be methyl group and this R can be methyl group, it is known as poly beta hydroxyl butyrate.

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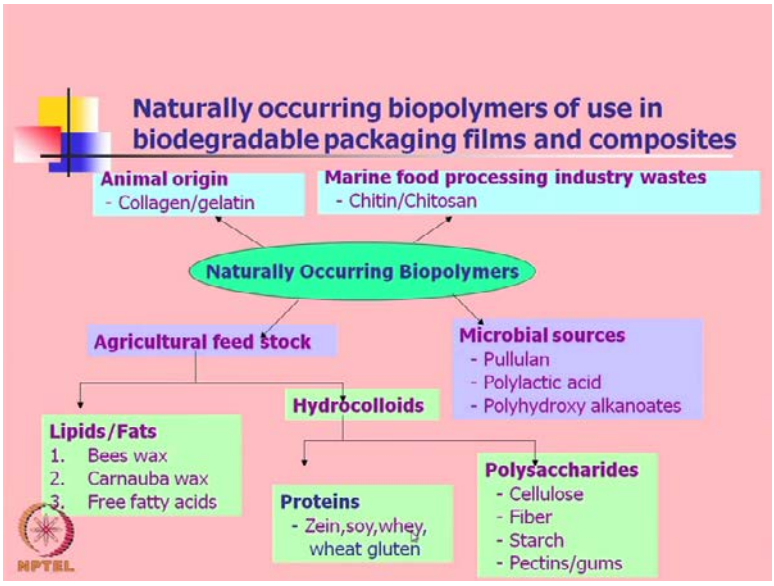

Now, let us look into naturally occurring biopolymers of use in biodegradable packaging films and composites. Naturally occurring biopolymers are animal origin, can say collagen and gelatine. Now, collagen can be harvested from animal source.

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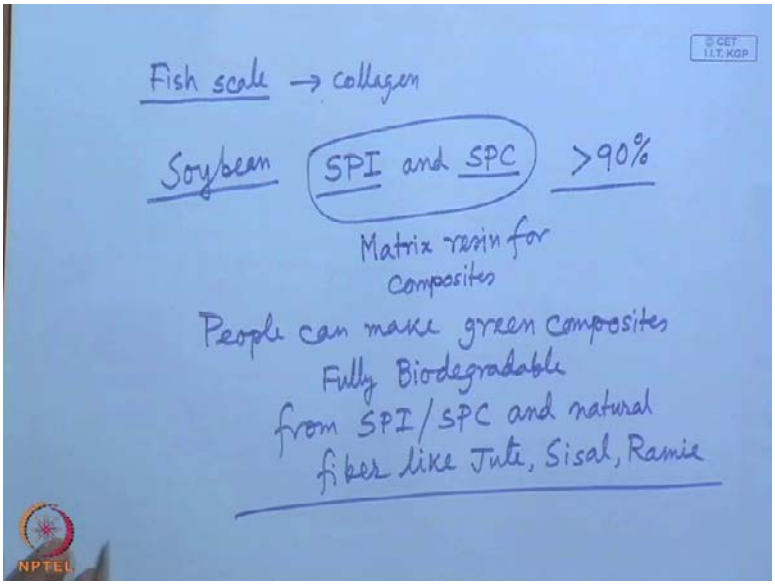

Say we can take of fish scale. This fish scale contains a good amount of collagen, that collagen can be harvested from fish scale or other animals. Marine food industries waste, they process such chitin and chitosan and other polymers are from natural source lipids and fats from agricultural stocks or hydrocolloids. Now, under lipids and fats, we see these are bees wax, carnauba wax, free fatty acids can be evaluate from agricultural stocks or proteins are zein, soy, whey, wheat gluten. These can be obtained from agricultural stocks as well as these polysaccharides or cellulose, fibre, starch and pectin can be available from agriculture stocks.

Microbial sources we can get pullulan, poly lactic acid, poly hydroxyl alkanoates these things. Now, regarding this soy actually, soy be, we just seen it from which we can get a oil, we can get protein. Now from soybean there are two kinds of proteins available, one soy protein isolate SPI and soy protein concentrate SPC. Now, the protein content in this two different soybean products are very high more than 90 percent. Very good matrix size SPA and SPC, these polymers are very good matrix resin for making composites. People can make green composites, which a fully bio degradable from such SPA or SPC and some natural fibre like jute, sisal and ramie. Other than this soy protein can also be highlighted

and another form what we have developed in our laboratory, that is soy milk. Directly squeezed out from white soy milk and this soy milk is... In fact we have used this soy milk as a matrix resin or jute based green composite.

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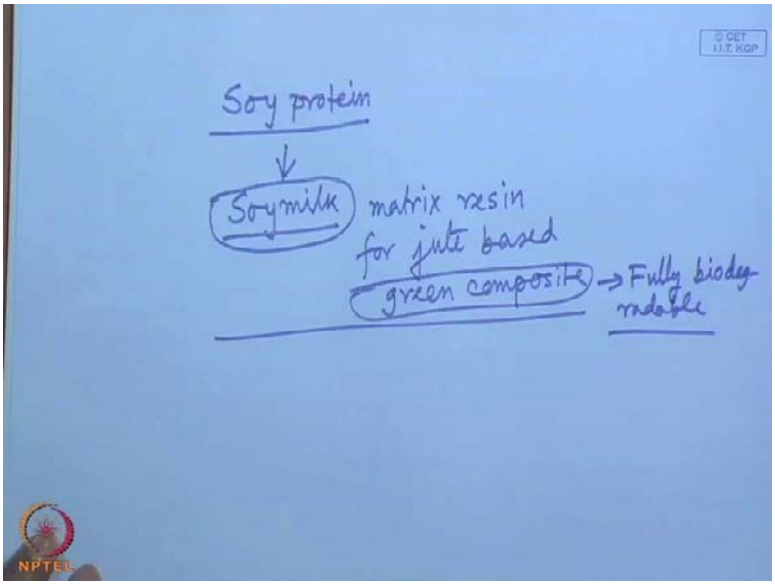

We are found this green composite as filly bio degradable, fully bio degradable. So, here we see naturally occurring biopolymers from animal source, agricultural source or microbial source. We got lot of different products can be made, which we can use for a bio degradable formation, bio degradable manufacturing.

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This major technology development for manufacture products are echo sufficient, echo efficient sustainable biodegradable plastics; and in biodegradable plastics technology, we can use aliphatic polyesters and copolymers, poly lactic acid and polymers, starch and starch esters, other starch derivatives. And we can developed starch foam technology, we can make combination of caprolactone or poly caprolactone, which is synthetic polymer. That can combined with starch, so these starch poly (( )) caprolactone blend can be used for making bio degradable products. Let us stop here; we will do the rest of part in the next lecture.

Thank you.