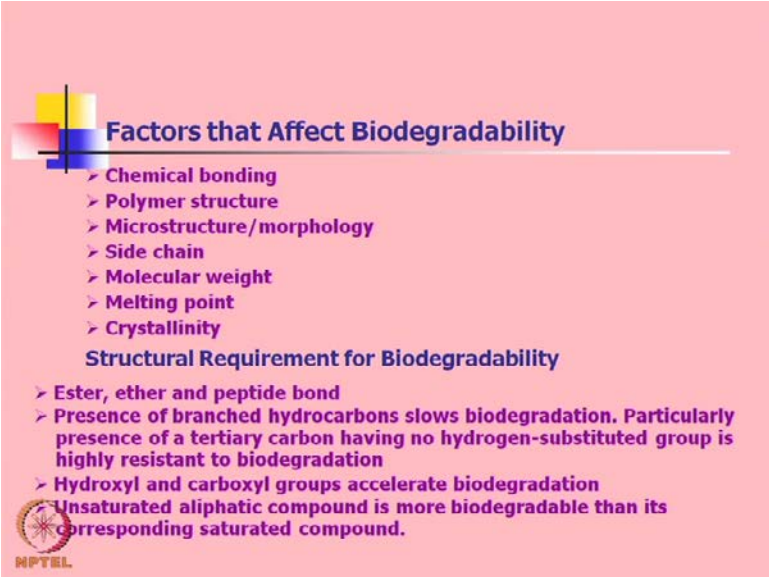
Science and Technology of polymers
Prof. Basudam Adhikari
Department of Material Science
Indian Institute of Technology, Kanpur

Lecture - 31
Environmental Degradation of Polymers (Contd.)

(Refer Slide Time: 00:24)



Factors that Affect Biodegradability

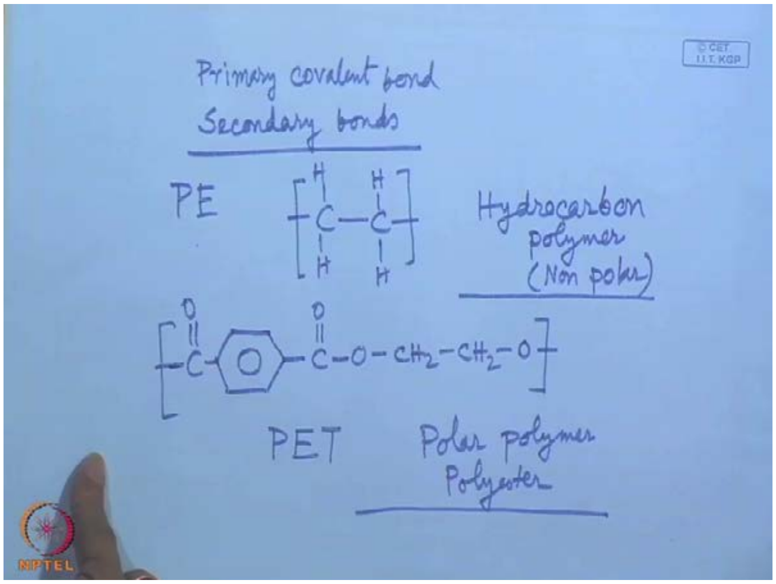
- Chemical bonding
- Polymer structure
- Microstructure/morphology
- Side chain
- Molecular weight
- Melting point
- Crystallinity

Structural Requirement for Biodegradability

- Ester, ether and peptide bond
- Presence of branched hydrocarbons slows biodegradation. Particularly presence of a tertiary carbon having no hydrogen-substituted group is highly resistant to biodegradation
- Hydroxyl and carboxyl groups accelerate biodegradation
- Unsaturated aliphatic compound is more biodegradable than its corresponding saturated compound.

Now we were discussing about the biodegradation of polymer products now, let us discuss about the various factors, which are responsible for biodegradation, biodegradation of such polymers. These factors, the most important factor is chemical bonding in polymers that means nature of bonding, nature of chemical bonding.

(Refer Slide Time: 00:53)



Primary covalent bond
Secondary bonds

PE

Hydrocarbon polymer (Non polar)

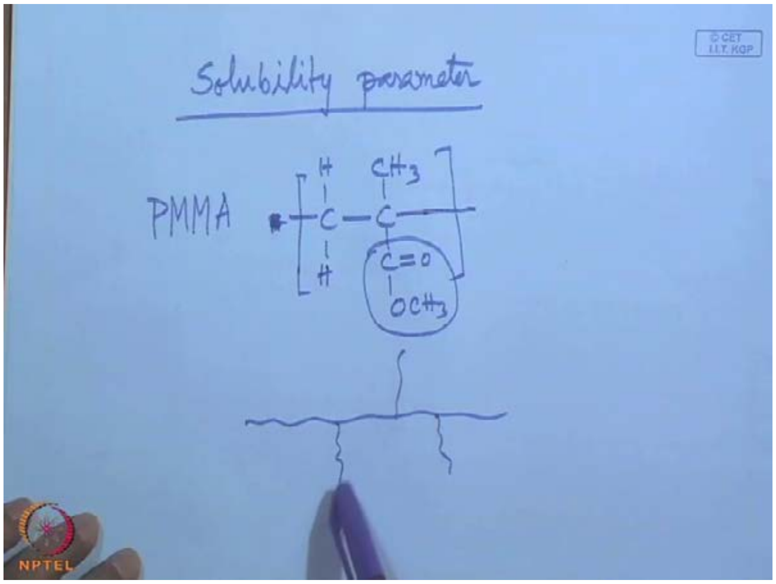
PET

Polar polymer
Polyester

Chemical bonding I mean say, as I told a primary covalent bonds and secondary bonds. It will be clear, if we think of this polyethylene, polyethylene having this kind of bonding. This is the repeat unit of polyethylene. Here you find primary covalent bond between carbons, primary covalent bond between hydrogens. There can be other kind of bond say having this kind of, this is the repeat unit formula of polyethylene terephthalate; this is polyethylene, this is polyethylene terephthalate polyester.

This is hydrocarbon polymer, it is non polar, this is polar polymer, this polyester. It you compare the nature of bonding between these two polymers apart from carbon to carbon bond, apart from carbon to hydrogen bonds, there are bonds like carbon to oxygen, single bond, single covalent bond and carbon to oxygen double bond and carbon to oxygen single bond in the backbone chain. So, degradation performance of these two polymers are totally different, this polymer is considered as non degradable polymer in the environment, this is a degradable polymer in the environment. So, we have to think of what kind of bond is present in chemical bond is present in which polymers, what kind of secondary bonds are present, what kind of, what is the total quantity of secondary bond is present, so that is related to solubility parameter of the polymer.

(Refer Slide Time: 04:01)



So, these are all correlated. This solubility parameter can also give some hints about the effect of this chemical bonding on solubility on the polymer, strength of the polymer and the degradability etcetera. Then polymer structure; polymer structure if we again think of these two polymers - polyethylene and polyethylene terephthalate; the structures are different. So, the degradation phenomenon is also different in these two polymers. Then what about the micro structure and morphology?

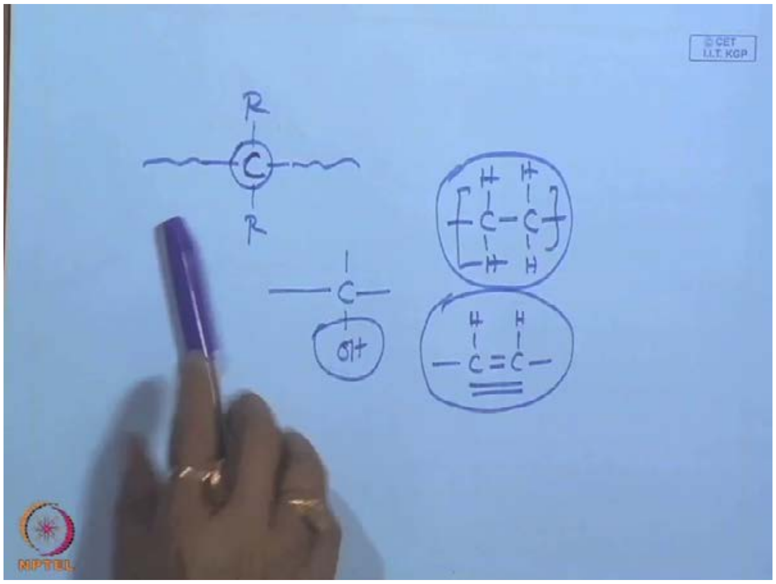
Micro structure means that in the solid state these polymers are normally the polymers are amorphous in nature, but there are polymers which are semi crystalline or crystalline polymers means if there is long range order in polymers as is found in case of polymer, polyethylene, this is a semi crystalline polymer whose crystallinity can vary from 40 percent to 60 percent to 70 percent crystalline percentage and the rest is amorphous. So, this is semi crystalline polymer, this can also be crystalline polymer if it is developed in the form of fiber.

Similarly, nylon that is also a crystalline polymer; so that if that polymer contains crystalline structure we can say, we say the micro structure is crystalline as well as their morphology, then side chains. Now, there can be polymers like say PMMA polymethyl methacrylate. Its formula is this sorry, this is substituent or you can say side chain or a polymer can have we show this configuration while it can have a side chain or branch like this so that whether the polymer contains side chain or not, if the, whether the side chain is polar in nature or non polar in nature, this is a polar side chain, this is a non polar side chain or side group etcetera.

So, that also influence the biodegradation or degradation by organisms. Molecular weight, if the molecular weight is very high again the degradation will be lower. So, molecular weight is also a parameter or a factor you must think of. Melting point, high melting point polymers or the polymers which actually melt at the high temperature, those are not degradable very easily, that takes longer time; whether, polymers having lower melting point, lower softing range they degrade faster.

Similarly, the crystallinity which is related to this micro structure and morphology etcetera. And let us think of other structure requirements which I have already pointed out. Say, polymers containing these ester groups, ether groups and peptide functional groups, they are degradable. Now, presence of branched hydrocarbons means side chains that slow down the biodegradation process particularly, the presence of a tertiary carbon atom.

(Refer Slide Time: 08:00)



Tertiary carbon atom means this carbon polymer chain is a carbon, carbon atom. Now, this can be attached to groups like these. So, this carbon is called tertiary carbon. Now, if the polymer contains a tertiary carbon having no hydrogen substituted group is highly registered to biodegradation. Hydroxyl and carboxyl groups, presence of hydroxyl or carboxyl group along the backbone chain of the polymer like this that accelerates biodegradation. Now, unsaturated aliphatic compound is more biodegradable than its corresponding saturated compound. That is why this polyethylene having this saturated backbone chain like this; this is not degradable whereas if a polymer chain contains unsaturated bonds like this, other groups are there. So, if such type of bond is present in the polymer backbone chain so such polymer will be degraded faster than the polymers having a saturated structure.

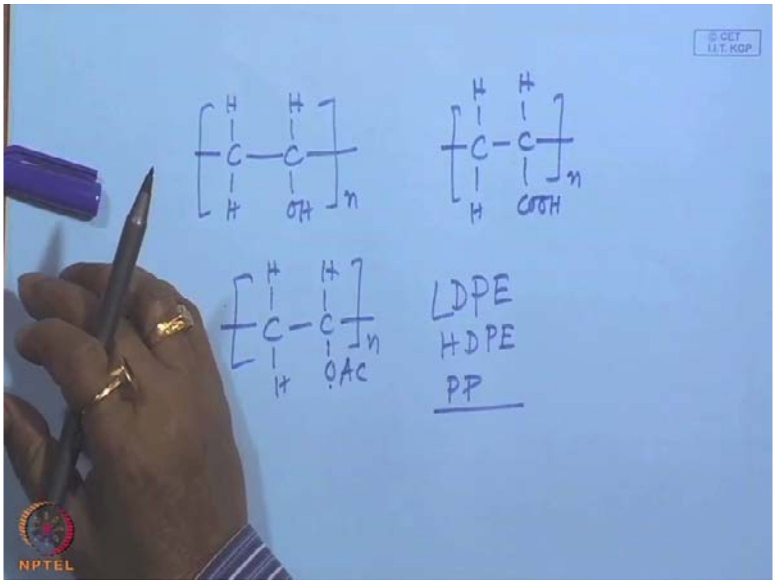
(Refer Slide Time: 09:28)

Trends Towards Relative Biodegradability of Polymers

Aliphatic > alicyclic > aromatic
Hydrophillic > hydrophobic
Low mol. wt. > High mol. wt.
Low melting > high melting
Amorphous > crystalline

Now, the order of biodegradation of polymers say aliphatic polymer will be more degradable than polymers which are alicyclic in nature than aromatic in nature. So, aromatic polymers are less degradable than aliphatic polymers. Similarly, a polymer if it is hydrophilic means hydrophilic means water loving polymer whose surface can be wetted by water or which can mix up with water etcetera.

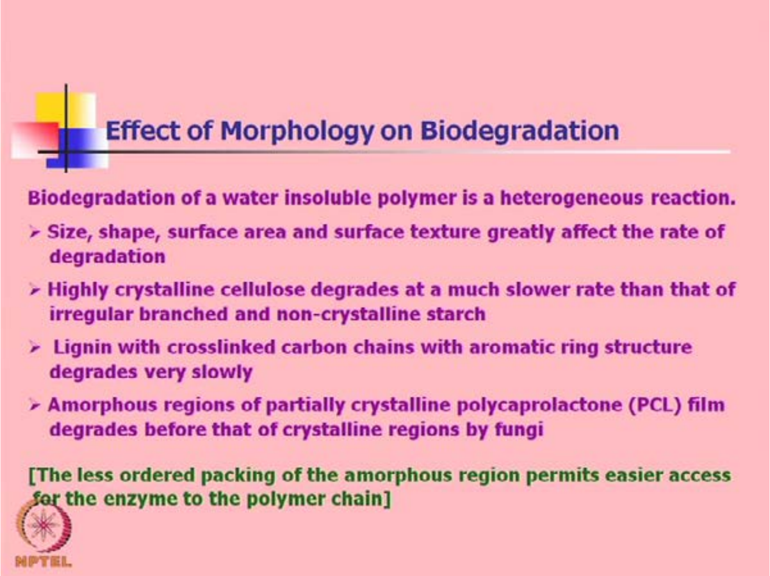
(Refer Slide Time: 10:09)



These are known as hydrophilic polymer for example say polyvinyl alcohol is a hydrophilic polymer, this is polyvinyl alcohol. This is hydrophilic polymer, it dissolves in water, it is a water solute polymer, this is degradable. Similarly, say polymer like this is again hydrophilic polyacrylic acid, this is again hydrophilic. This also biodegradable, similarly polyvinyl acetate, this is again biodegradable. So, this is, these are all hydrophilic polymers whereas polyethylene say LDPE or HDPE high density polyethyene or polypropylene these are hydrophobic polymers, these are non degradable.

So, hydrophilic polymers are more degradable polymers than hydrophobic polymers; polymers having low molecular weight is more degradable than high molecular weight. Polymers having lower melting point, lower sharpening range, sharpening point than higher melting point will be more degradable. Amorphous polymers are more degradable than crystalline polymers. This is because, this is because this crystalline polymers are compact due to the molecular alignment the space, free space in between the molecules, inter molecular space is less where this water cannot penetrate or the chemicals cannot diffuse inside or even or even the micro organisms cannot go inside the crystalline polymers whereas amorphous polymers having more free space through which these can go inside the bulk of the polymer and that degrades faster.

(Refer Slide Time: 12:15)



Effect of Morphology on Biodegradation

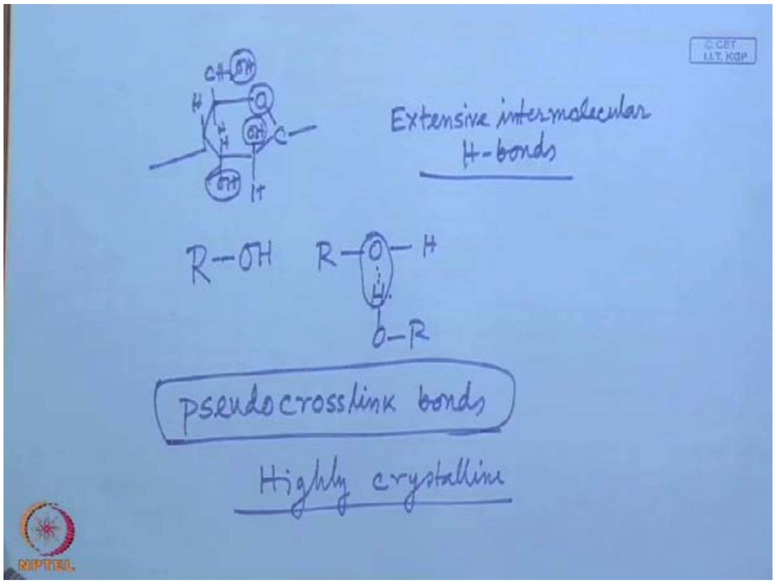
Biodegradation of a water insoluble polymer is a heterogeneous reaction.

- Size, shape, surface area and surface texture greatly affect the rate of degradation
- Highly crystalline cellulose degrades at a much slower rate than that of irregular branched and non-crystalline starch
- Lignin with crosslinked carbon chains with aromatic ring structure degrades very slowly
- Amorphous regions of partially crystalline polycaprolactone (PCL) film degrades before that of crystalline regions by fungi

[The less ordered packing of the amorphous region permits easier access for the enzyme to the polymer chain]

So, that is why amorphous polyesters are more degradable or faster degradable than crystalline polymers. The effect of morphology on biodegradation, as I pointed out that morphology or microstructure, these are also influential parameter for biodegradation of polymers. Now, biodegradation of a water insoluble polymer is a heterogeneous reaction. Size, shape, surface area and surface texture greatly affect the rate of degradation of the polymers. Highly crystalline cellulose degrades at a much slower rate than that of irregular branched and non crystalline starch. Highly crystalline cellulose means that cellulose molecules, cellulose molecule say it looks like this.

(Refer Slide Time: 13:00)



Extensive intermolecular H-bonds

pseudocrosslink bonds

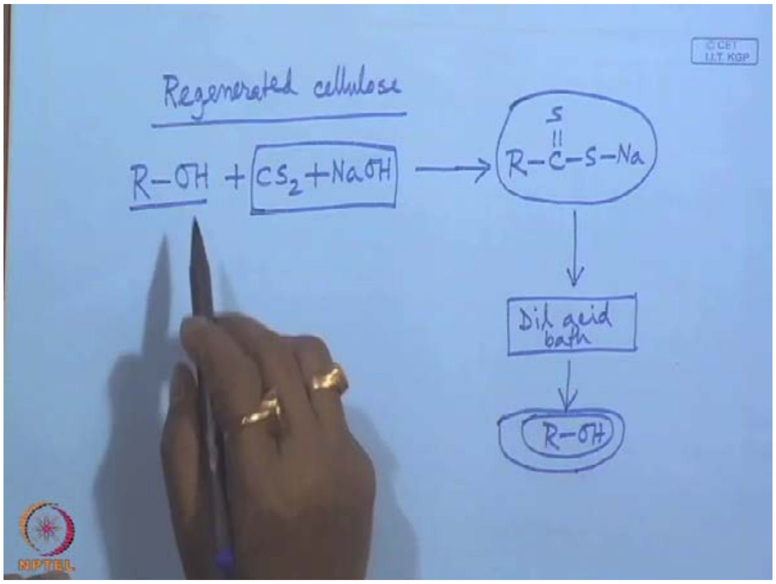
Highly crystalline

So, these are all carbons. So, this is primary hydrocellulose hydrogen, secondary hydroxyl group O H, H, H. So, it counters a nitro, a nitro glucose unit, it contains a nitro glucose unit that a nitro glucose unit, it contains this hydroxyl groups, primary and secondary hydroxyl groups as well as this oxygen atom over here. So, due to the presence of this hydroxyl groups there can be inter molecular hydrogen bonds. So, if we represent this cellulose as R O H. Now, this R O H you can write other way O H. Another, R O H can be written this way.

So, this oxygen hydrogen can form initiate this hydrogen bond. So, in case of cellulose there is extensive inter molecular hydrogen bonds. Now, this intermolecular, intermolecular hydrogen bonds present in cellulose that behaves like pseudo crosslink bonds. So, pseudo crosslink bonds means this are, there is intimate bonding between the cellulose a nitro glucose units of each a nitro glucose unit of one molecule with other a nitro glucose unit of the other molecules.

So, that does not help the polymers to be more hydrophilic and that prevents biodegradation. So, (( )) is that is called actually that due to that hydrogen bond that cellulose molecule becomes highly crystalline. So, highly crystalline cellulose degrades at a much slower rate than that of irregular branched and non crystalline starch. So, if the crystallinity in cellulose can be reduced by some chemical treatments say we can say the regenerated cellulose.

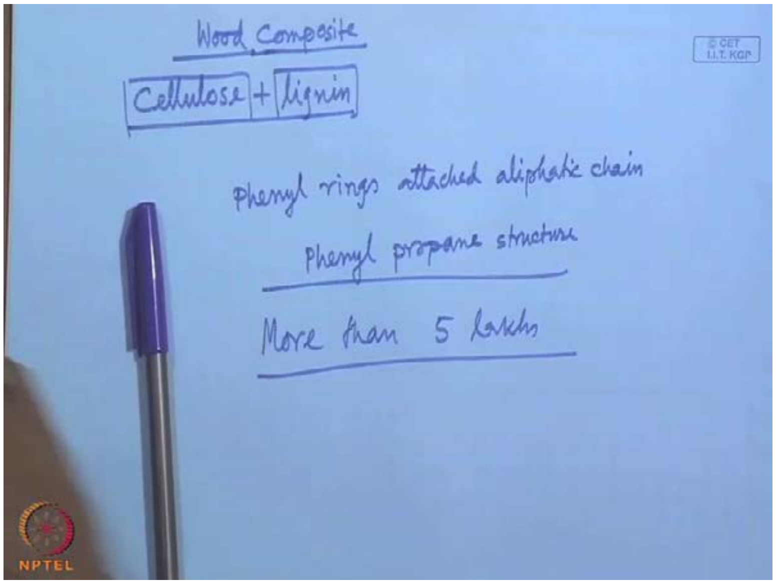
(Refer Slide Time: 16:05)



These are the cellulose; regenerated cellulose is these are the cellulose. This is prepared by cellulose R O H. Now, in one of the techniques of different regeneration processes say this is one, say it is reacted with carbon disulphide and sodium hydroxide, it forms sodium cellulose (( )). This is (( )) that means cellulose cab be cellulised, dissolved in carbon disulphide, aqueous solution of carbon disulphide and sodium hydroxide. It forms a viscous solution in water then if it is put in acid bath say dilute acid bath say sulfuric acid, dilute sulfuric acid, cellulose will be regenerated; that this process of treatment of cellulose with carbon disulphide and sodium alkali and then reprecipitation in acid bath.

It gets back, gives back this cellulose. In this case, the hydrogen bonds, the number of hydrogen bonds in that cellulose is reduced. Here, it contains less number of hydrogen bonds; here it contains more number of hydrogen bonds. So, this becomes soft and that is more hydrophilic and that is more degradable than the cellulose which are the original cellulose molecule, original cellulose material. Lignin with cross linked carbon chains with aromatic ring structure degrades very slowly. Now, lignin is a molecule that is a polymer, lignin is a polymeric material. That lignin occurs in nature in food as a matrix material.

(Refer Slide Time: 18:33)



Wood Composite

Cellulose + lignin

Phenyl rings attached aliphatic chain

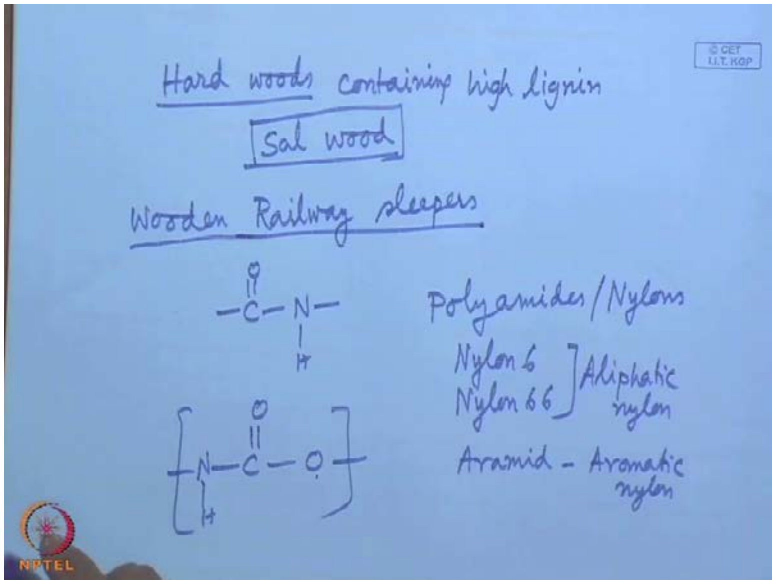
Phenyl propane structure

More than 5 lakhs

Cellulose plus lignin makes the wood that means wood is basically, wood is basically made of cellulose and lignin where cellulose is a fiber and lignin is the matrix and this forms this wood composite. This lignin contains some phenyl rings attached to aliphatic chain. Basically, these are the derivatives of phenyl propane net, phenyl propane structure and that is a joint molecule, lot of linkages between such phenyl propane units and the molecular rate becomes more than 5 lakhs.

So, that is the high molecular rate lignin and that lignin when cross linked with carbon chains, with aromatic ring structure etcetera that also degrades very slowly, that is why. Not only that, this phenyl propane structure and it contains some phenol, phenolic groups. Due to the presence of phenyl groups, this phenolic groups are that prevents, phenolic groups prevent oxidity degradation.

(Refer Slide Time: 20:53)

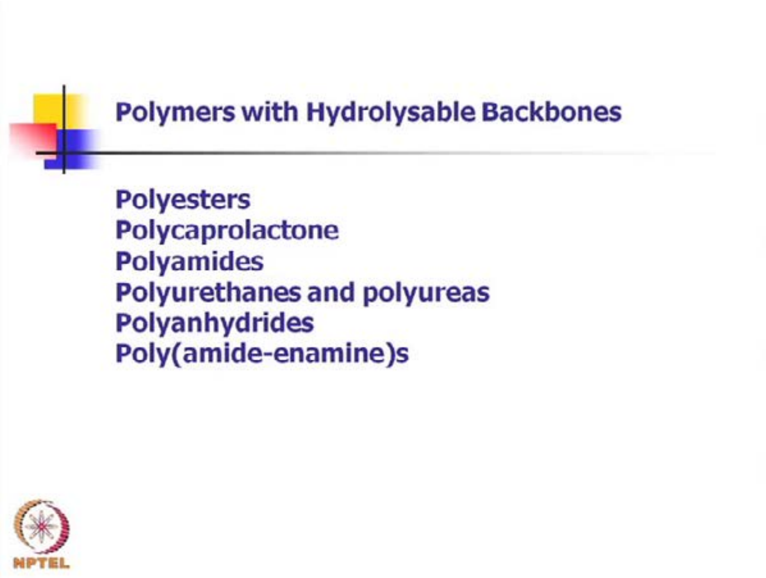


That is why we see that hard woods, hard woods. Earlier, this hard woods containing high lignin percent, high lignin content, containing high, containing high lignin amount, I want to, lignin say Sal wood. This is heavy wood, this is very heavy, density is very high, it is also very strong and you know this Sal woods were used as railway sleepers. Today, railway sleepers have been, wooden railway sleepers are replace by steel sleepers than concrete sleepers. Today, almost entire railway track as been replaced, replaced with this concrete, reinforced concrete sleepers, (( )) this Sal wood.

Now, that was exposed to, that was remaining exposed to environment, open environment, outer environment in contact with soil, in contact with air, in contact with heat, sunlight etcetera still those are not so easily degradable and the life of those wooden sleepers are very high. That is due to the presence high quantity of lignin which contains those phenyl rings and phenol units which actually act as anti oxidants or anti degradients in wood. So, it is true that if a polymer contains lignin that polymer will be stable, it will not degrade.

So, that degrades whereas, unit degrades, that degrades very slowly and wooden furniture, the life of wooden furniture is so high because of the presence of lignin in wood material. Amorphous regions of polymers of partially crystalline polycaprolactone say partially crystalline polycaprolactone film degrades before that of crystalline regions by fungi. So, it is, it has been established that a polymer if it is amorphous, it will be degraded faster.

(Refer Slide Time: 23:38)



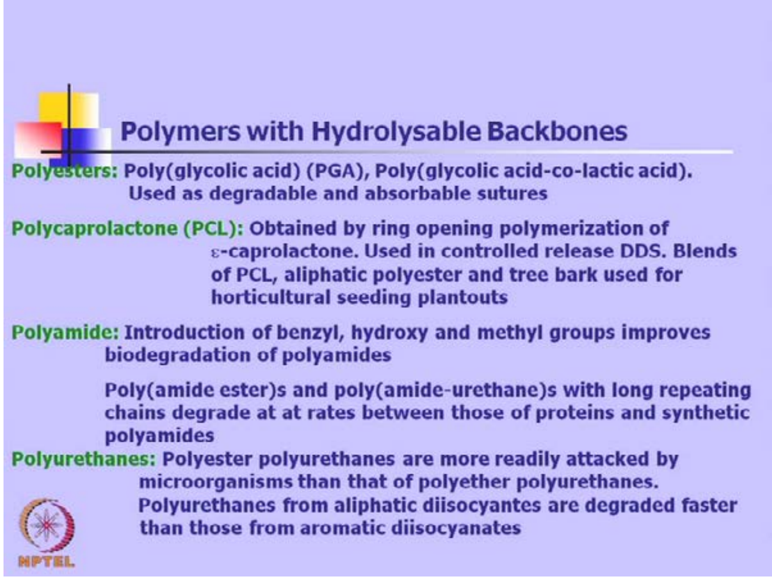
Polymers with Hydrolysable Backbones

Polyesters
Polycaprolactone
Polyamides
Polyurethanes and polyureas
Polyanhydrides
Poly(amide-enamine)s

Now, let us see the examples of polymers having hydrolysable backbones which can be degraded by hydrolysis. So, these are polyesters, polycaprolactone, polycaprolactone, this also another kind of synthetic polyester made from epsilon caprolactone (( )) polymerization. Poly amides having peptide linkage, peptide links in proteins, this is peptide linkage which is present in proteins, same linkage is present in polyamides or nylons, say nylon 6, nylon 66 or this is, these are aliphatic nylon. There can be aramid which is aromatic nylon.

Now, aliphatic nylon degrades faster than aromatic nylon. So, these nylons are in general known as polyamides because of the presence of this amide linkage which is similar to that of peptide linkage in proteins. Polyurethanes and polyureas, polyurethanes containing linkage like this, this is polyurethane linkage having nitrogen, oxygen, along with carbon and hydrogen in the polymer chain, polyureas etcetera, polyanhydrides, polyamide enamines, polyamide imides etcetera. So, these polymers are degraded by hydrolysis. So, there are known as hydrolysable polymers.

(Refer Slide Time: 25:55)



Polymers with Hydrolysable Backbones

Polyesters: Poly(glycolic acid) (PGA), Poly(glycolic acid-co-lactic acid). Used as degradable and absorbable sutures

Polycaprolactone (PCL): Obtained by ring opening polymerization of ε-caprolactone. Used in controlled release DDS. Blends of PCL, aliphatic polyester and tree bark used for horticultural seeding plantouts

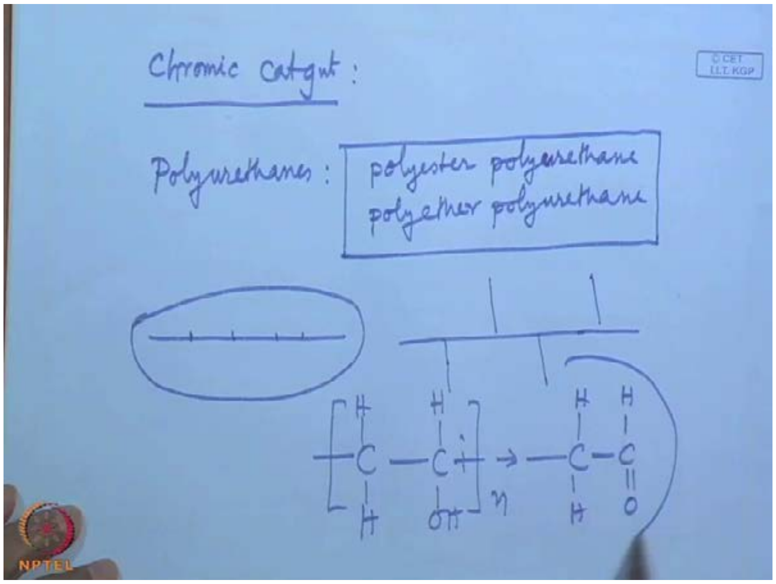
Polyamide: Introduction of benzyl, hydroxy and methyl groups improves biodegradation of polyamides

Poly(amide ester)s and poly(amide-urethane)s with long repeating chains degrade at at rates between those of proteins and synthetic polyamides

Polyurethanes: Polyester polyurethanes are more readily attacked by microorganisms than that of polyether polyurethanes. Polyurethanes from aliphatic diisocyantes are degraded faster than those from aromatic diisocyanates

So, again typical examples of hydrolysable polymers are polyesters, say poly glycolic acid. This is a synthetic polymer. Poly glycolic acid co lactic acid say co polymer. These are used as degradable and absorbable sutures. Now, after surgery the, after surgery it needs to be, two parts needs to be joined by stitching with sutures.

(Refer Slide Time: 26:42)



Chromic catgut :

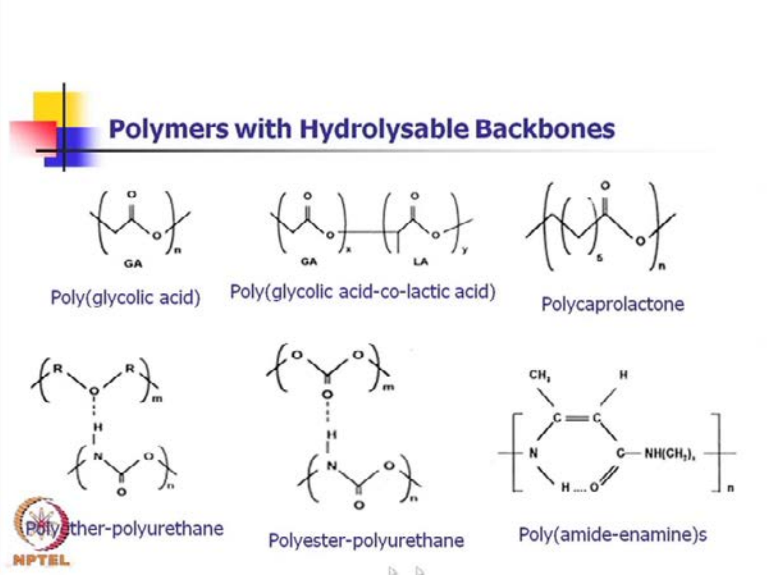
Polyurethanes : polyester polyurethane
polyether polyurethane

Previously, chromic catgut made of sheep intestine submucosa. This chromic catgut is not degradable. So, after surgery and stitching when the wound heels then it needs to be removed by a second surgery which becomes painful to the patient. Now, today bio absorbable, biodegradable sutures have been developed from this poly glycolic acid or poly glycolic acid poly lactic acid co polymer or poly lactic acid which slowly degrades within the body and the degradation products gets absorbed within the body without any hazards or toxic effects on to the living system.

So, these synthetic polymers are very good biodegradable or bio absorbable polymers and after 7 to 15 days depending on the natures of wounds, nature of healing time etcetera so these polymers slowly gets dissolved, gets absorbed within the body and by that time wound heals. Polycaprolactone, this is obtained by ring opening polymerization of caprolactone used in controlled release of drug delivery system. Blends of polycaprolactone, aliphatic polyester and tree bark are used for horticultural seeding plant outs.

Polyamides, in polyamide introduction of benzyl group, hydroxyl group or methyl group that improves biodegradation of polyamides, polyamide esters, these are ester amides. That means a polymer containing both amide linkage and ester linkage which are both hydrolysable or amide linkage or urethane linkage which are both hydrolysable. So, polyamide ester or poly amide urethanes with long repeating, repeating chains that degrades at rates between those of proteins and synthetic polyamides. Polyester polyurethanes are also readily attacked by microorganisms and hydrolysable degraded and then the polyether polyurethanes these are also degradable. So, polyurethanes can be, polyurethanes can be polyester polyurethane or polyether polyurethane. Both polymers are degradable either by microbes or through hydrolyte path.

(Refer Slide Time: 29:56)



Polymers with Hydrolysable Backbones

Poly(glycolic acid)

Poly(glycolic acid-co-lactic acid)

Polycaprolactone

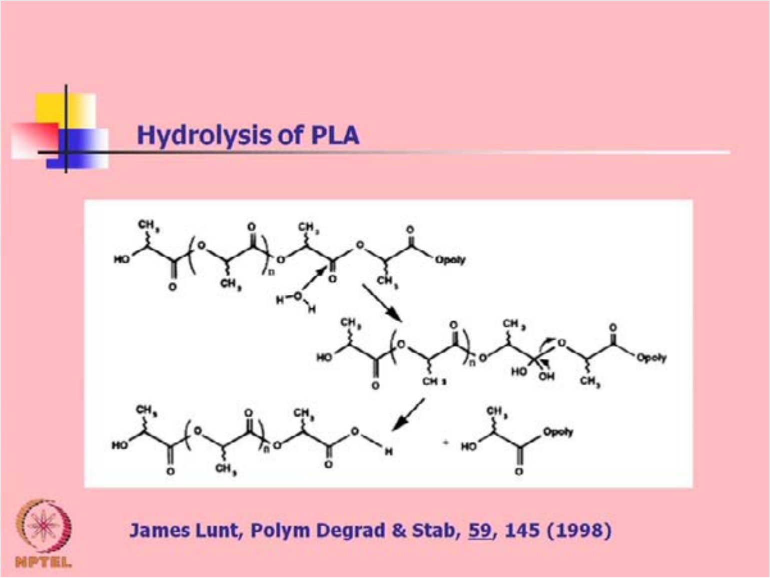
Polyether-polyurethane

Polyester-polyurethane

Poly(amide-enamine)s

Now, here there are the structures of those polymers, poly glycolic acid, poly glycolic acid lactic acid, polycaprolactones, polyether polyurethanes, they are having intermolecular hydrogen bonds and polyamide enamines. If you look into the structure you can understand why they will be degradable by microorganisms or they will be degraded by the action of acids or alkalis through hydrolysis.

(Refer Slide Time: 30:37)

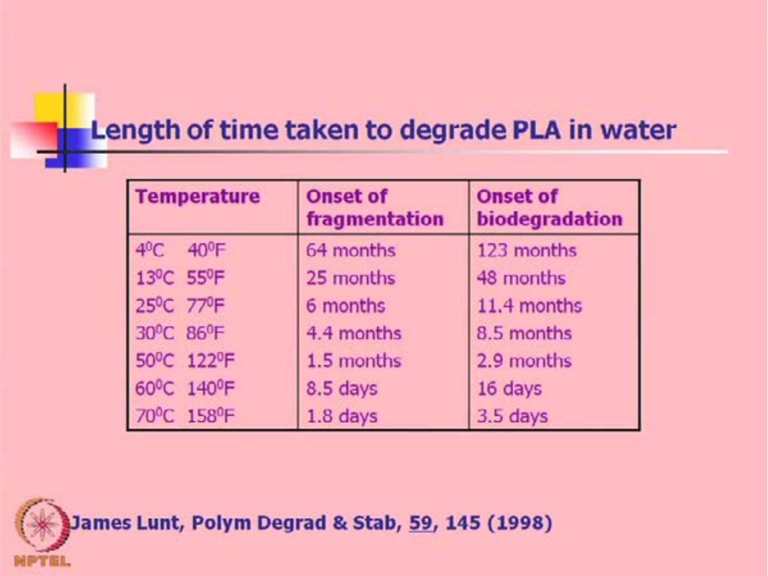


Hydrolysis of PLA

James Lunt, Polym Degrad & Stab, 59, 145 (1998)

This shows a scheme of reaction which occurs during hydrolysis of polylactic acid. This contains ester group, this is the reaction how it degrades. Ultimately, this is the fragments, this is the products of degradation, this is one product. So, after fragmentation this smaller, small length species will be formed which will be easy for the microorganisms to metabolize.

(Refer Slide Time: 31:11)



Length of time taken to degrade PLA in water

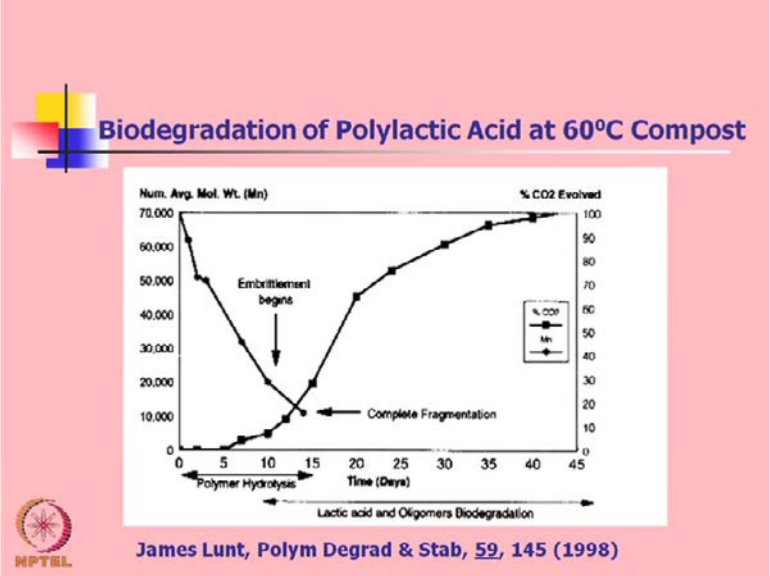
Temperature	Onset of fragmentation	Onset of biodegradation
4^0C 40^0F	64 months	123 months
13^0C 55^0F	25 months	48 months
25^0C 77^0F	6 months	11.4 months
30^0C 86^0F	4.4 months	8.5 months
50^0C 122^0F	1.5 months	2.9 months
60^0C 140^0F	8.5 days	16 days
70^0C 158^0F	1.8 days	3.5 days

James Lunt, Polym Degrad & Stab, 59, 145 (1998)

Length of time taken to degrade poly lactic acid in water, some experiments are carried out. This is the reference of this work published in Polymer Degradation and Stability at different temperatures, the onset of fragmentation. What happens during degradation? First of all the polymers get fragmented into smaller lengths. After fragmentation through hydrolysis of those hydrolysable bonds then microorganisms can perform at a faster rate. So, this shows the time period at different temperatures say if you do the degradation for fragmentation at lower temperature, the time requirement is quite high.

Whereas, if the temperature is increased this fragmentation will be very faster from 64 months to it has come down to say 2 days, around 2 days and onset of biodegradation again at what temperature? It is very long as I mentioned that in high altitude area where the temperature is very low sometimes sub zero temperature, their the, even the nights are does not degrade, forget about the degradation of polymer materials. But, if the temperature is increased the degradation is much faster from such 123 months to three and half to 4 days time.

(Refer Slide Time: 32:56)

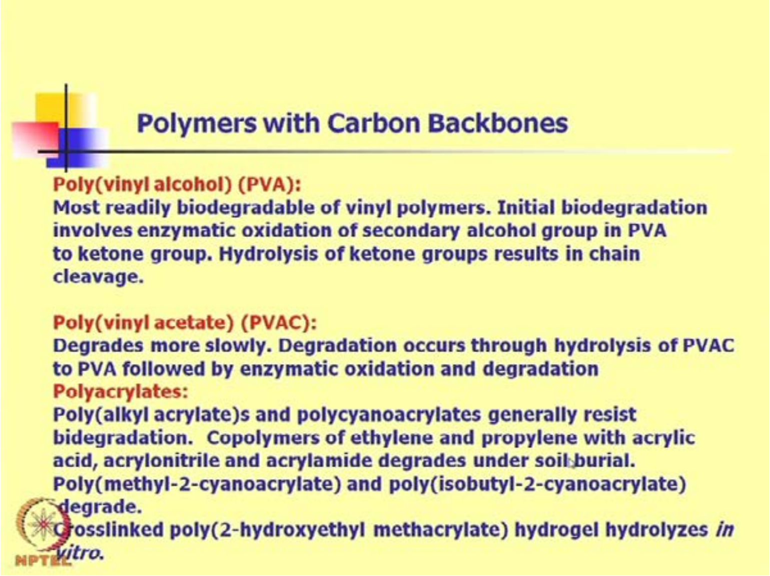


Biodegradation of Polylactic Acid at 60°C Compost

James Lunt, Polym Degrad & Stab, 59, 145 (1998)

This shows the decrease of molecular weight with time during degradation as well as evolution of carbon dioxide due to biodegradation of the polymer. Now, here in this period of time say 10 days, within 10 days time embrittlement of the polymer to fragmentation it starts and ultimately between 10 to, after 15 days there it has been found that the polylactic acid was completely fragmented at 60 degree Celsius temperature in compost condition and you see the molecular weight has come down of 70,000 average molecular weight to almost 10,000 molecular weight as species of 10,000 molecular weight fragments.

(Refer Slide Time: 34:12)



Polymers with Carbon Backbones

Poly(vinyl alcohol) (PVA):
Most readily biodegradable of vinyl polymers. Initial biodegradation involves enzymatic oxidation of secondary alcohol group in PVA to ketone group. Hydrolysis of ketone groups results in chain cleavage.

Poly(vinyl acetate) (PVAC):
Degrades more slowly. Degradation occurs through hydrolysis of PVAC to PVA followed by enzymatic oxidation and degradation

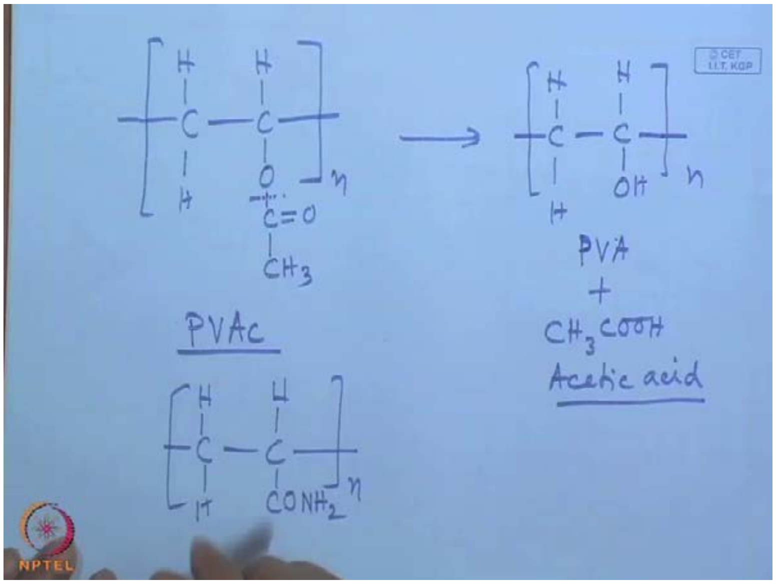
Polyacrylates:
Poly(alkyl acrylate)s and polycyanoacrylates generally resist bidegradation. Copolymers of ethylene and propylene with acrylic acid, acrylonitrile and acrylamide degrades under soil burial.
Poly(methyl-2-cyanoacrylate) and poly(isobutyl-2-cyanoacrylate) degrade.
Crosslinked poly(2-hydroxyethyl methacrylate) hydrogel hydrolyzes *in vitro*.

And it shows almost complete bio degradation, 100 percent bio degradation in 40 to 45 days time period. Polymer with carbon backbones, these are also degradable. So, I showed that polymers containing such degradable groups like ester, ether, amide in the, along the backbone chain is one kind and other kind is the branched or side chains like this. So, we have discussed polymers of this type where the degradable groups, functional groups say ester, ether, amide etcetera were present along the backbone.

Here, two such groups are present in the pendant groups as such or the side chains. These are say polyvinyl alcohol; I have shown you the formula polyvinyl alcohol. Once again, we can say that is this polyvinyl alcohol, this polyvinyl alcohol, this polyvinyl alcohol PVA, most readily biodegradable vinyl polymer. Initial biodegradation involves enzymatic oxidation of secondary alcohol group, this is the secondary alcohol group in PVA to ketone group. It is converted to ketonic group like this. So, it breaks, it will break over here and form a ketone.

So, fragmented polymer. So, ketonic groups, hydrolysis of ketone group results in chain cleavage. So, gradually hydroxyl groups is converted to ketone then ketone groups resulting chain cleavage. In case of polyvinyl acetate that degrades more slowly and degradation occurs through hydrolysis of polyvinyl acetate to PVA followed by enzymatic oxidation and degradation.

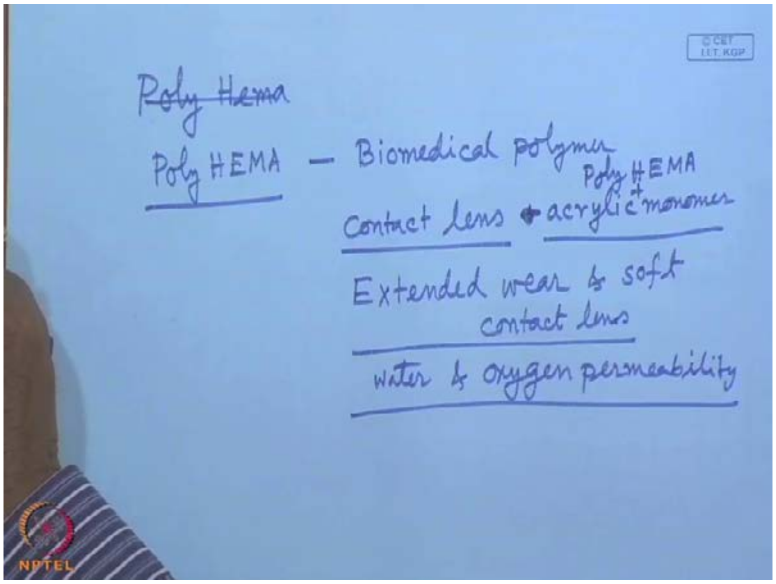
(Refer Slide Time: 36:32)



Say, this is polyvinyl acetate. This is the repeat unit of polyvinyl acetate, you can write this way also, polyvinyl acetate. Now, this is the vulnerable bond where it can utilize forming this polyvinyl alcohol, polyvinyl alcohol and acetic acid; so first this acetate group. This acetate group will be hydrolyzed followed by enzymatic oxidation and degradation of this polyvinyl alcohol. So, because of this first step of hydrolysis then degradation it takes longer time or degrades slowly.

Polyacrylates, poly alkyl acrylate and polycyanoacrylates generally resist biodegradation. Copolymers of ethylene and propylene with acrylic acid, acrylonitrile and acrylamide degrades under soil burial. Acrylamide is this polymer, this is water solvable polymer. This acrylamide, this monomer this portion can be copolymerized with ethylene or other vinyl monomers or we can have poly alkyl cyanoacrylates say poly isobutyl cyanoacrylates, poly methyl cyanoacrylate. We can have polymers of say acrylic acid and acrylonitrile. So, these polymers degrade slowly by micro organisms or hydrolytic duration. Crosslinked poly 2 hydroxyethyl methacrylate hydrogel hydrolyzes in vitro. Now, this is actually this poly 2 hydroxyethyl methacrylate.

(Refer Slide Time: 39:43)



~~Poly Hema~~

Poly HEMA — Biomedical polymer

Contact lens + Poly HEMA + acrylic monomer

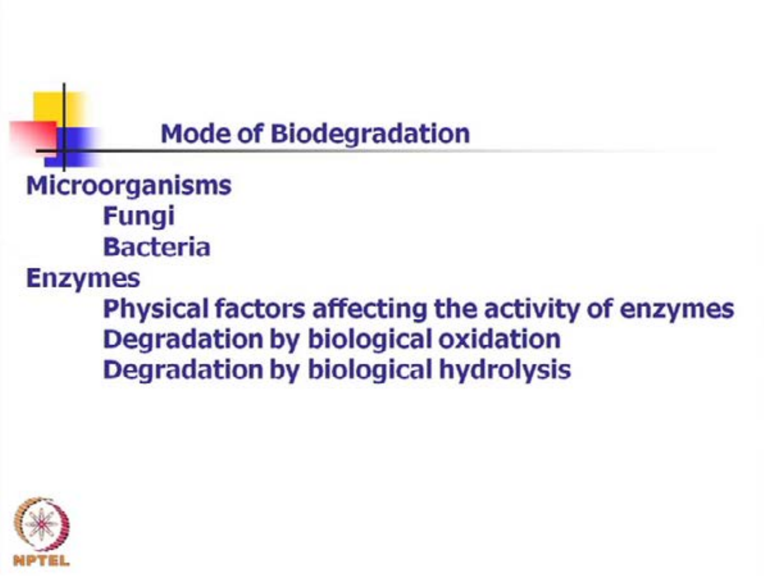
Extended wear & soft contact lens

water & oxygen permeability

This is known as poly HEMA, if there is hydroxy methyl group this is called poly HEMA. Hydroxy ethyl or sorry I should write this way, poly HEMA H E M A, poly hydroxy ethyl methacrylate, polyhydroxyethylmethacrylate it is poly HEMA. This poly HEMA, this is very good bio medical polymer. This is used to make contact lens along with other acrylic monomer.

So, a copolymer of some other acrylic monomer and this poly HEMA sorry poly HEMA and other hydroxyethylmetha copolymer of hydroxyethylmethacrylate and acrylic monomer forms good contact lens which can be very extended wear and soft contact lens which provides facility of water and oxygen permeability. Now, this crosslink poly HEMA is a very good hydrogel. This crosslinked poly HEMA is very good hydrogen and that hydrogen can be used for drug delivery device also.

(Refer Slide Time: 41:59)

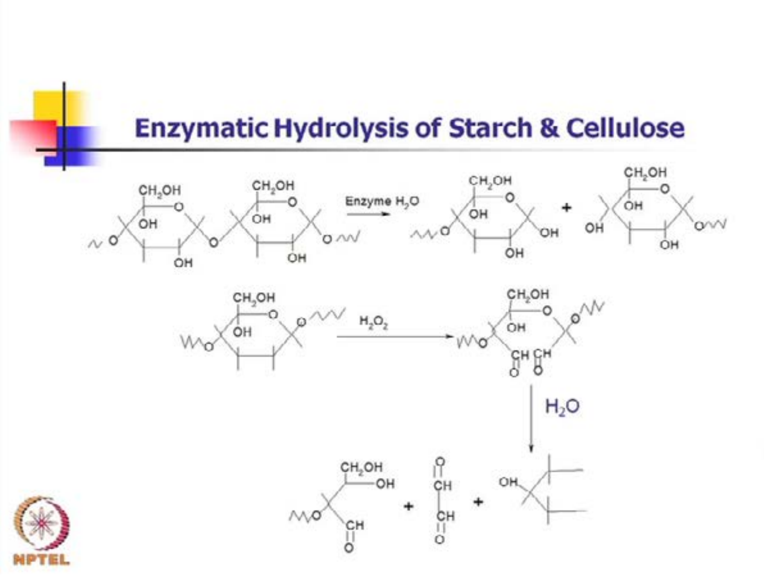


Mode of Biodegradation

Microorganisms
  Fungi
  Bacteria
Enzymes
  Physical factors affecting the activity of enzymes
  Degradation by biological oxidation
  Degradation by biological hydrolysis

Modes of biodegradation are by micro microorganisms say fungi, bacteria. Enzymatic degradation where physical factors affects the activity of enzymes, degradation by biological oxidation, degradation by biological hydrolysis, so all these three are influenced by enzymes whereas this fungi and bacteria can also degrade polymers.

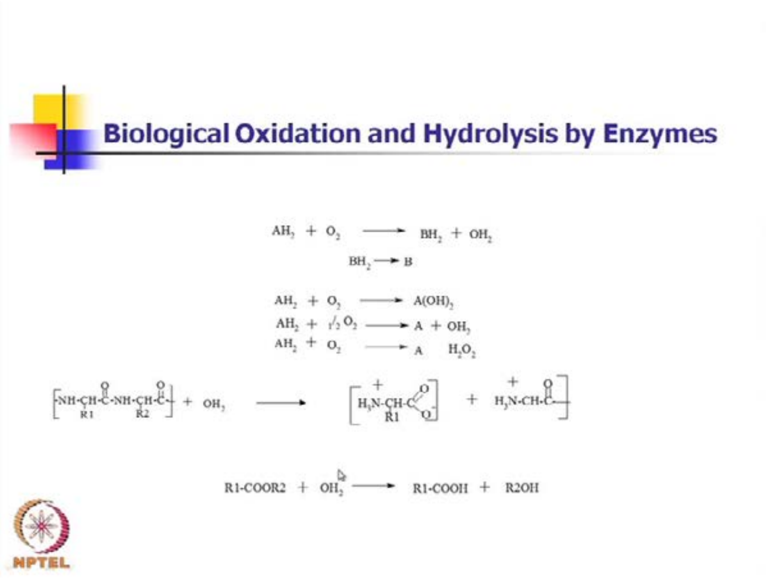
(Refer Slide Time: 42:30)



Enzymatic Hydrolysis of Starch & Cellulose

This shows a chemical scheme, reaction scheme for enzymatic hydrolysis of starch and cellulose. This is the anhydroglucose unit of starch or cellulose. Now, enzyme in water that breaks this linkage forming fragments that means the molecular rate of this polymers is almost reduced to half if there is one action of enzyme at this bond. Similarly, more action of enzymes can fragment a cellulose molecule or starch molecule to many such numbers of this anhydroglucose units with hydroxyl groups at one end. So, this way we can degrade the starch and cellulose polymers.

(Refer Slide Time: 43:23)



Biological Oxidation and Hydrolysis by Enzymes

$$AH_2 + O_2 \longrightarrow BH_2 + OH_2$$

$$BH_2 \longrightarrow B$$

$$AH_2 + O_2 \longrightarrow A(OH)_2$$

$$AH_2 + 1/2\,O_2 \longrightarrow A + OH_2$$

$$AH_2 + O_2 \longrightarrow A \quad H_2O_2$$

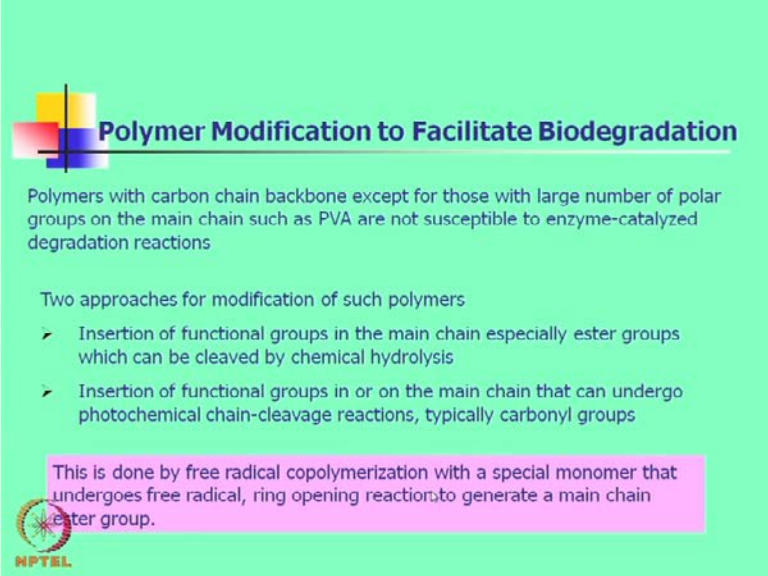
$$\left[\text{NH-}\underset{R1}{\text{CH}}\text{-}\overset{O}{\overset{\|}{C}}\text{-NH-}\underset{R2}{\text{CH}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\right] + OH_2 \longrightarrow \left[\overset{+}{H_3N}\text{-}\underset{R1}{\text{CH}}\text{-C}\begin{smallmatrix}O\\ O^-\end{smallmatrix}\right] + \left[\overset{+}{H_3N}\text{-CH-}\overset{O}{\overset{\|}{C}}\text{-}\right]$$

$$R1\text{-}COOR2 + OH_2 \longrightarrow R1\text{-}COOH + R2OH$$

NPTEL

And biological oxidation and hydrolysis by enzymes, this is, this shows a scheme of reaction, scheme of reaction that is basically this is oxidation process. This oxidation reaction is catalyzed by the presence of enzymes and heat actually produces ultimately acids and alcohols if the polymer is a polyester. So, this is my degradation of polyesters by the action of enzyme, basically it is oxidation process, enzymatic oxidation process that produces fragments containing acids and alcohol groups. So, the products would become acidic in nature.

(Refer Slide Time: 44:13)



Polymer Modification to Facilitate Biodegradation

Polymers with carbon chain backbone except for those with large number of polar groups on the main chain such as PVA are not susceptible to enzyme-catalyzed degradation reactions

Two approaches for modification of such polymers

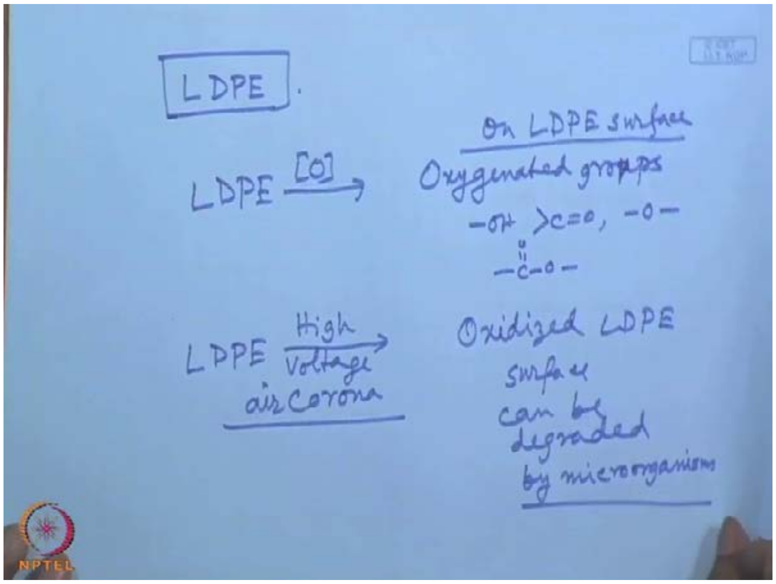
- Insertion of functional groups in the main chain especially ester groups which can be cleaved by chemical hydrolysis
- Insertion of functional groups in or on the main chain that can undergo photochemical chain-cleavage reactions, typically carbonyl groups

This is done by free radical copolymerization with a special monomer that undergoes free radical, ring opening reaction to generate a main chain ester group.

Now, polymers can also be converted to biodegradable nature, non biodegradable to biodegradable in nature through chemical modification. Say, polymers with chain carbon with backbone except for those with large number of polar groups on the main chain such as PVA are not susceptible to enzyme catalyzed degradation reactions. In this connection we can discuss that say LDPE films which are used as packaging films, as carry bag films which are creating a lot of nuisance in the environment, this films are flying here and there, littering here and there on the road side or the garbage side.

So, which is actually creating lot of nuisance and problems in the environment to the society also; so this we cannot avoid. The use of such LDPE films as packaging films or carry bags we cannot avoid, we have to use, but we must think of certain process which can degrade this films, carry bag films after it is thrown to the garbage. Now, as I mentioned the surface energy of this polymers are such that the contact length is very high, the bacteria cannot sit on the surfaces, but if this surface, if the surface of such LDPE films can made polar means the oxygenation, this can be oxidized by some means, oxidized by some means for some oxygenated group like say O H group or ketonic group or ether group or ester group etcetera. If this could be created on the surface of this LDPE by (( )) through oxidation, by means of oxidation then such LDPE can be degraded by microorganisms.

(Refer Slide Time: 46:40)



LDPE

$\text{LDPE} \xrightarrow{[O]}$ Oxygenated groups

On LDPE surface

$-OH$, $>C{=}O$, $-O-$

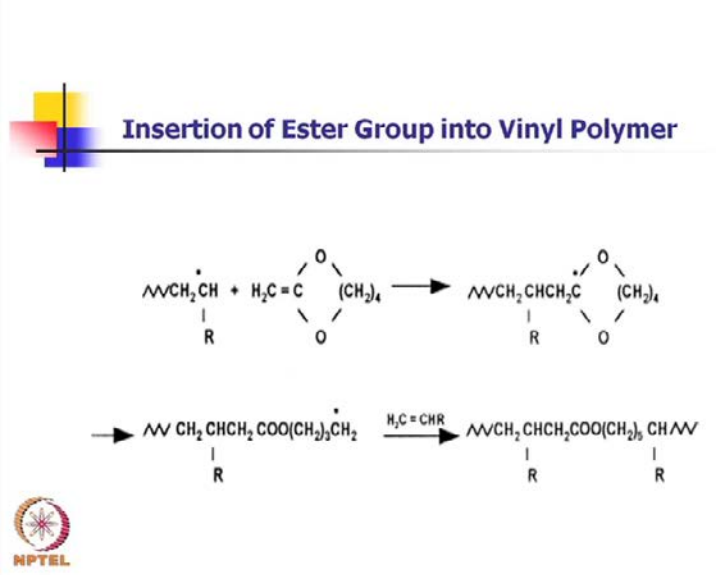
$-\overset{O}{\overset{\|}{C}}-O-$

$\text{LDPE} \xrightarrow[\text{air corona}]{\text{High Voltage}}$ Oxidized LDPE surface can be degraded by microorganisms

So, that is a kind of modification. So, if this LDPE can be exposed to corona, high voltage corona. Say, air corona so that air contains oxygen, high oxygenated, highly active oxygenated species will impinge on the LDPE surface and this LDPE surface should be oxidized. That oxidized LDPE surface can be degraded by microorganisms or bacteria as well as fungi. That is possible, we have done some experiments, we have seen that yes, it is working, it is functioning so that technology can be developed.

So, there are two approaches for modification of such polymers, insertion of functional groups in the main chain especially ester groups as I mentioned which can be cleaved by chemical hydrolysis or insertion of functional groups in or on the main chain that can undergo photochemical chain cleavage reactions, typically carbonyl groups. This is done by free radical copolymerization with a special monomer that undergoes free radical ring opening reaction to generate a main chain ester group. So, there is possibility of converting non degradable hydro carbon type of polymers which will be degradable by microorganisms by chemical modification on their surface.

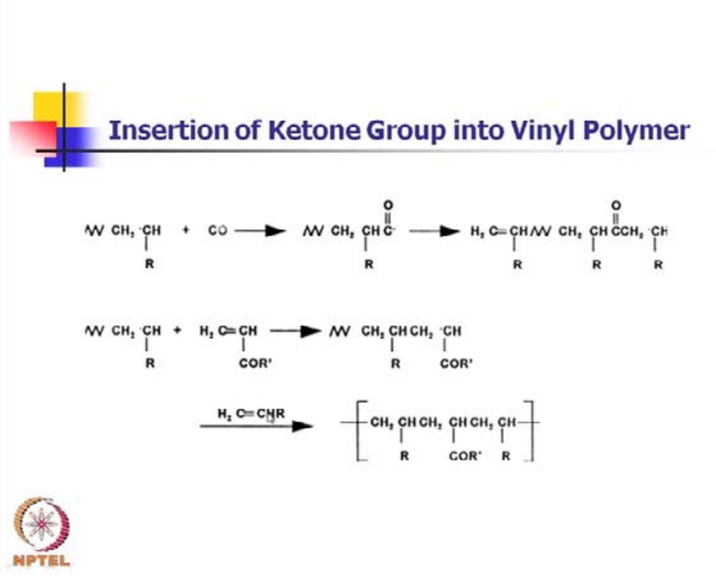
(Refer Slide Time: 48:35)



Insertion of Ester Group into Vinyl Polymer

So, here shows the reaction scheme, reaction scheme which is basically insertion of some ester group on to a vinyl polymer like this where you see some ester group has been inserted in a vinyl polymer and this vinyl polymer being a hydrocarbon in nature adding only carbon carbon backbone chain. Now, that has been converted to a carbon chain with some oxygen atom and ketonic group, ester group on the backbone chain. So, COO has been inserted in the backbone chain. So, that vinyl polymer will be degradable by this process if it is modified.

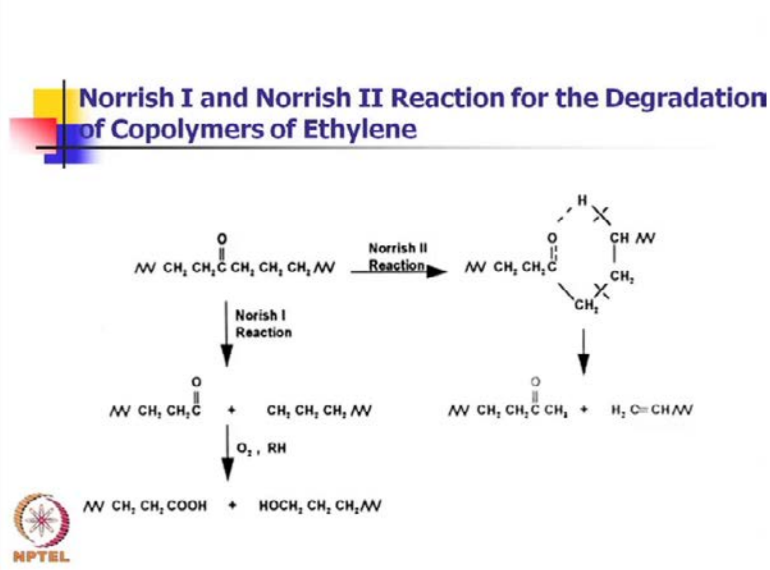
(Refer Slide Time: 49:22)



Insertion of Ketone Group into Vinyl Polymer

Similarly, ketone group can also be inserted in vinyl polymer and here you see some CO group has been inserted by this way of chemical reaction and such insertion of ketone group can also help degradation of vinyl polymers.

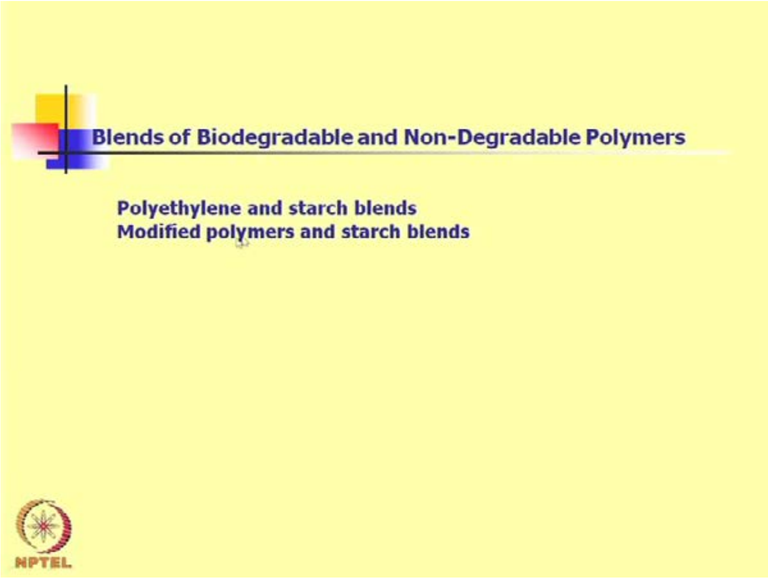
(Refer Slide Time: 49:45)



Norrish I and Norrish II Reaction for the Degradation of Copolymers of Ethylene

Basically, as I mentioned that if a polymer surface can be oxygenated means oxygen atoms in the form of ketone, ester, hydroxyl or ether if such type of groups can be created on the surfaces of polymer that polymer will be degradable by hydrolysis or by microorganisms. Now, this again shows another kind of reactions scheme known as Norrish one and Norrish two reaction mechanism for the degradation of copolymers of ethylene. Norrish one path and this is the Norrish two path and ultimately these are the your fragmented products forming from a polyester molecule we can get fragments having groups like carboxyl on acidic group as well hydroxyl group, alcohol group. So, a polyester bond after breaking it will form carboxyl and hydroxyl groups and polymer chain will be fragmented into many parts.

(Refer Slide Time: 50:53)

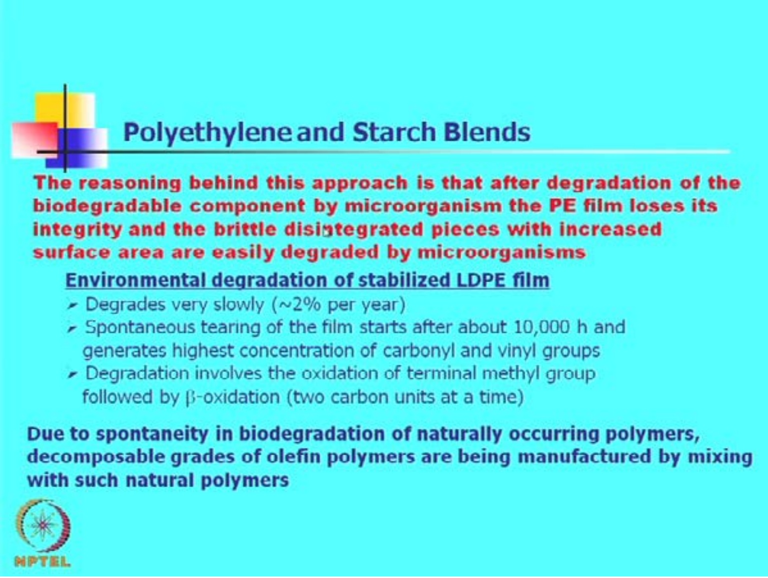


Blends of Biodegradable and Non-Degradable Polymers

Polyethylene and starch blends
Modified polymers and starch blends

Then otherwise and means of developing biodegradable polymers are by blending a non degradable polymer with a degradable polymer, say polyethylene is a non degradable polymer and that can be degraded, this polyethylene polymer can be degraded by blending with starch. People have taken ventures today, available. This kind of product is also available in the market. This polyethylene starch film or modified polymers can also be modified; chemically modified polymers and starch can be blended to form some biodegradable polymer. Actually, agriculture (( )) films are been produced from blending of, by blending of polyethylene with starch.

(Refer Slide Time: 51:39)



Polyethylene and Starch Blends

The reasoning behind this approach is that after degradation of the biodegradable component by microorganism the PE film loses its integrity and the brittle disintegrated pieces with increased surface area are easily degraded by microorganisms

Environmental degradation of stabilized LDPE film

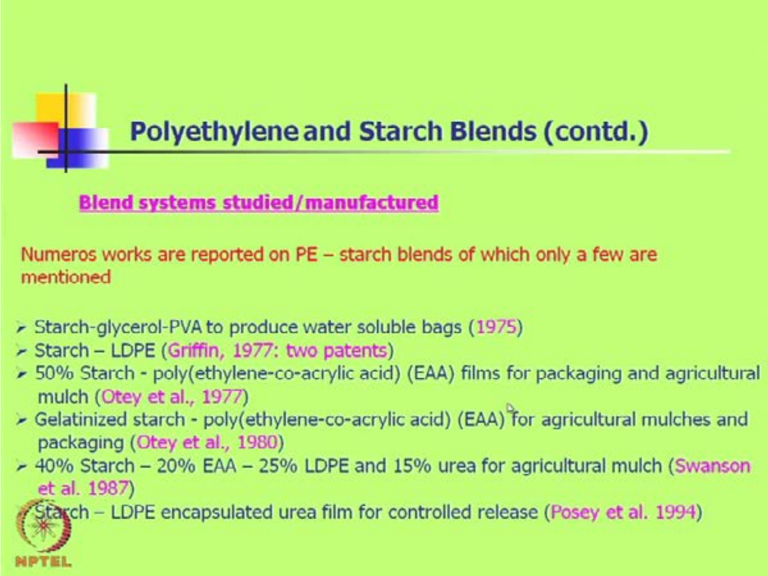
- Degrades very slowly (~2% per year)
- Spontaneous tearing of the film starts after about 10,000 h and generates highest concentration of carbonyl and vinyl groups
- Degradation involves the oxidation of terminal methyl group followed by β-oxidation (two carbon units at a time)

Due to spontaneity in biodegradation of naturally occurring polymers, decomposable grades of olefin polymers are being manufactured by mixing with such natural polymers

Now, the reasoning behind this approach of blending starch with your polyethylene is that after degradation of the biodegradable component of the microorganism by microorganism, say if starch is incorporated there starch is a very good excellent food for microbes. So, starch will be eaten which is, which remains dispersed in, within the polymer film and ultimately what happens? This your starch will be eaten up and the polymer film will be porous and it can be easily fragmented into smaller pieces, disintegrated into smaller pieces and surface area will be increased and microorganism will degrade the film very, at a very faster rate.

Now, without, there are some LDPE films which are used today for packaging, these are stabilized with some stabilizers anti oxygen etcetera that degrades very, at a very slow rate, say at 2 percent per year. And spontaneous tearing of such film occurs after 10,000 hour of composed condition, composed degradation. Then degradation involves the oxidation of terminal methyl group followed by beta oxidation. This is the mechanism of degradation, how this stabilized LDPE film degrades, but that is very slow process and that is, we cannot consider such type of stabilized films as degradable polymers.

(Refer Slide Time: 53:07)



Polyethylene and Starch Blends (contd.)

Blend systems studied/manufactured

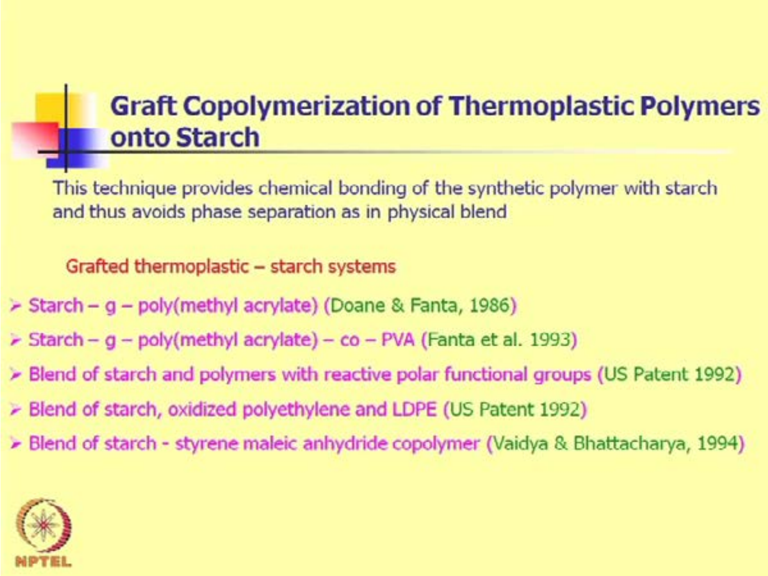
Numeros works are reported on PE – starch blends of which only a few are mentioned

- Starch-glycerol-PVA to produce water soluble bags (1975)
- Starch – LDPE (Griffin, 1977: two patents)
- 50% Starch - poly(ethylene-co-acrylic acid) (EAA) films for packaging and agricultural mulch (Otey et al., 1977)
- Gelatinized starch - poly(ethylene-co-acrylic acid) (EAA) for agricultural mulches and packaging (Otey et al., 1980)
- 40% Starch – 20% EAA – 25% LDPE and 15% urea for agricultural mulch (Swanson et al. 1987)
- Starch – LDPE encapsulated urea film for controlled release (Posey et al. 1994)

So, they are blend systems available and already which have been manufactured and products are available in the market. These are the systems, starch, glycerol, polyvinyl alcohol which produce water soluble bags which have been developed. Starch LDPE blend has been produced and patents have been taken on this process technology. 50 percent starch, polyethylene co acrylic acid polymer, acrylic acid ethylene copolymer with 50 percent starch that also have shown very good degradation properties and that has been used for packaging and agricultural mulch film.

Gelatinized starch was also blended with ethylene acrylic acid copolymer for agricultural mulche application or agricultural mulch application as well as packaging. 40 percent starch in 20 percent ethyl acrylic ethylene co acrylic acid polymer and 25 percent LDPE; so LDPE ethyline, ethylene acrylic acid copolymer and starch. So, 40, 20, 25, 15 percent urea which are actually some fertilizer is also included in this film which gives some slow release fertilizer action as well as degradation. This is for agriculture purpose. Starch LDPE encapsulated urea film was also used for controlled release of fertilize, control release, control release fertilizer films for agricultural applications.

(Refer Slide Time: 54:47)



Graft Copolymerization of Thermoplastic Polymers onto Starch

This technique provides chemical bonding of the synthetic polymer with starch and thus avoids phase separation as in physical blend

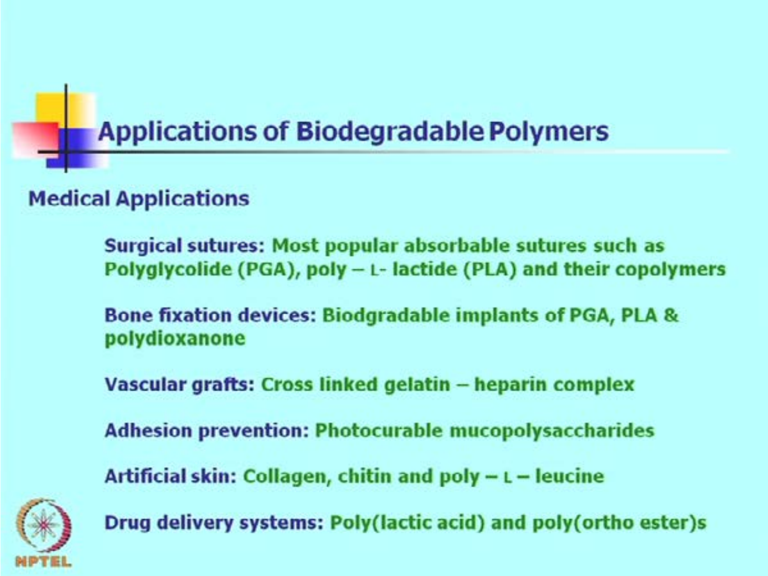
Grafted thermoplastic – starch systems

- Starch – g – poly(methyl acrylate) (Doane & Fanta, 1986)
- Starch – g – poly(methyl acrylate) – co – PVA (Fanta et al. 1993)
- Blend of starch and polymers with reactive polar functional groups (US Patent 1992)
- Blend of starch, oxidized polyethylene and LDPE (US Patent 1992)
- Blend of starch - styrene maleic anhydride copolymer (Vaidya & Bhattacharya, 1994)

Then polymers can also be modified for developing biodegradable polymers through copolymerization and graft copolymerization of thermoplastic polymers onto starch. So, sratch can be grafted with say thermoplastic polymers. So, some works have been done and some patents have also have been taken. Here is few examples, starch was grafted with poly methyl acrylate, polymethyl acrylate and starch was blended with polymers having reactive polar functional groups.

Starch was blended with polymers which are already oxidized to some extent. These are the oxidized polyethylene or LDPE. These are blended in starch. So, after oxidization of polyethylene this becomes little degradable and starch can be miscible with this thing. Otherwise, starch is difficult to mix with polyethylene that is why oxidized polyethylene was used for blending with starch and blends of starch styrene maleic maleic anhydride copolymer, that was also used, develop for making, preparing biodegradable films.

(Refer Slide Time: 55:59)



Applications of Biodegradable Polymers

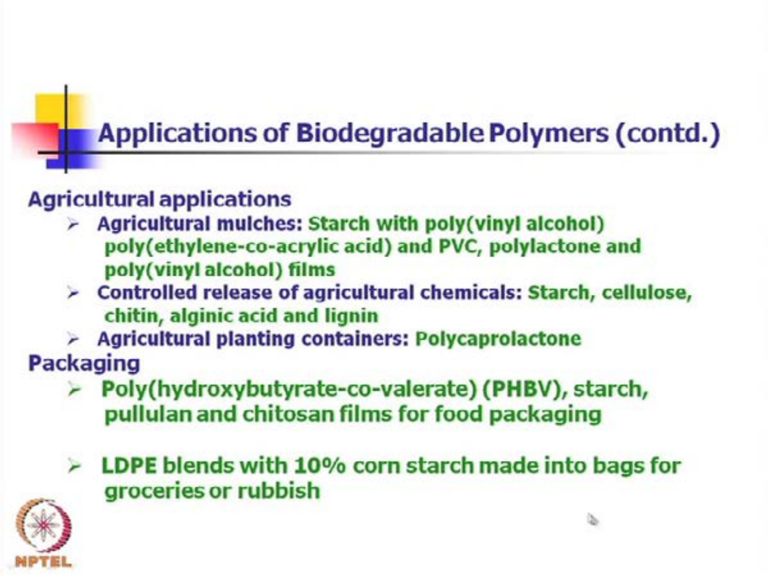
Medical Applications

- **Surgical sutures:** Most popular absorbable sutures such as Polyglycolide (PGA), poly – L- lactide (PLA) and their copolymers
- **Bone fixation devices:** Biodgradable implants of PGA, PLA & polydioxanone
- **Vascular grafts:** Cross linked gelatin – heparin complex
- **Adhesion prevention:** Photocurable mucopolysaccharides
- **Artificial skin:** Collagen, chitin and poly – L – leucine
- **Drug delivery systems:** Poly(lactic acid) and poly(ortho ester)s

NPTEL

And for the application of biodegradable polymers we can mention this surgical sutures is a most popular absorbable suture are poly glycolide PGA, poly L lactide PLA and their copolymers. These are used very good bio absorbable sutures. Bone fixation devices, say this bone fixation devices made from poly glycolide acid, poly lactic acid and polydioxanone along with other materials. Vascular grafts made from cross linked gelatin heparin complex. Adhesion prevention was also used during surgery. These are photocurable mucopolysaccharides which are used. Artificial skin was made from collagen, chitin and poly L leucine also. Collagen from fiscal, that can also be use for artificial as artificial skin. Drug delivery system say poly lactic acid and poly ortho esters are used for as drug delivery systems and other applications.

(Refer Slide Time: 57:06)



Applications of Biodegradable Polymers (contd.)

Agricultural applications

- **Agricultural mulches:** Starch with poly(vinyl alcohol) poly(ethylene-co-acrylic acid) and PVC, polylactone and poly(vinyl alcohol) films
- **Controlled release of agricultural chemicals:** Starch, cellulose, chitin, alginic acid and lignin
- **Agricultural planting containers:** Polycaprolactone

Packaging

- Poly(hydroxybutyrate-co-valerate) (PHBV), starch, pullulan and chitosan films for food packaging
- LDPE blends with 10% corn starch made into bags for groceries or rubbish

Agricultural applications, agricultural mulches already, I have mentioned. Controlled release of agricultural chemicals like say fertilizers and other pesticides, those are also can be incorporated in polymer for slow release. Agricultural planting containers say sapling pots etcetera have been also developed. Packaging films with poly hydroxybutyrate co valerate or starch, pullulan and chitosan films for food packaging. LDPE blends with 10 percent corn starch made into bags for groceries or rubbish films.

(Refer Slide Time: 57:41)

Conclusion

Essential Guidelines to Reach the Goal of Biodegradability

- Selection of a suitable polymer class
- Engineering essential structural units in the polymer
- Easy access of the polymer to the biodegradation agencies by the
    - Development of appropriate polymer texture having more exposed surface accessible to the degrading agencies
    - More hydrophilic and swelling morphology in moist environment
- Creating accelerated biodegradation environment
- Treating the degradable polymeric waste to rapid degradation in a Targeted Degradation Reactor at the expense of electrical or chemical energy
- Chemical modification of commodity polymers for biodegradation

And conclusion - essential guidelines to reach the goal of biodegradability, selection of a suitable polymer class, engineering essential structure units in the polymer. Easy access of the polymer to the biodegradation agencies by the development of appropriate polymer texture having more exposed surface accessible to the degrading agencies. Creating accelerated biodegradable, biodegradation environment and chemical modification of commodity polymers for biodegradation.

Thank you.