

# Biodegradable polymers: processes of degradation



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## **Introduction**

The ISO definition of a biodegradable polymer is “ an irreversible process leading to a significant change of the structure of a material, typically characterized by a loss of properties (e. g. integrity, molecular weight, structure or mechanical strength) and/or fragmentation. Degradation is affected by environmental conditions and proceeds over a period of time comprising one or more steps”

Biodegradable and compostable processes are essentially the same mechanism of how materials irreversibly breakdown into their fundamental composition, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub> and other low-molecular weight products. The major difference is on how they go about the decomposition, biodegradation occurs naturally where microorganisms metabolise the material, where as composting takes place under strict conditions & rate of degradation and the end product is non-toxic.

The process of composting will also be affected by the size of the particles, large pieces may not be compostable but shreds of the same material may be compostable. Materials can also be composted at homes and the end product used in gardening, but some materials may not be compostable at home and may require an industrial process.

Biodegradable and compostable polymers should not be confused with biopolymers, which are naturally occurring polymers that readily degrade in the environment, starch, cellulose, proteins are a few examples of biopolymers, while the former are polymers engineered to degrade in the environment through one or more mechanisms of degradation.

The degradation of a polymer should into consideration the other mechanisms of material degradation (oxidation, hydrolysis, photo-degradation, thermal-degradation) which can affect the polymer before or during the biodegradation process, or maybe the only mechanism acting on the polymer [ 41. wang ].

As more people are becoming more eco-conscious and aware of global warming, although not directly responsible, more effort is put into discovering new sustainable plastics and better manufacturability of these degradable polymers.

### **History and why bioplastics?**

The first polymers, or plastics as it generally known, recorded in history were produced by The Horners Company in London [BPF site] which used horn and tortoiseshell as the predominant early natural plastic in the year 1284. But it is in the early 18th century that the plastic industry started to build up its momentum, it is during the period Alexander Parkes invented the first plastic in the 1850's [makingthemodernworld]. Today polymers are the most widely used material playing in an important role in civil construction to human wellbeing.

A pair in Germany were awarded the patent to their invention of Casein Plastic as the first bioplastic derived from milk, but it was in 1990 that ICI Ltd launched the first commercially available biodegradable plastic.

With the world consumption of plastics increasing to 100 million tonnes annually , from 5 million tonnes in the 1950's,[M. Avella] and growing at a rate of 4% annually. They can only be recycled or dumped into a landfill,

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which are becoming scarce [J\_H\_Song] , and with more governments of the developed world taking advantage of the developing world, where they send their nations waste to be disposed to and where it cannot be dealt efficiently due to the lack of proper facilities. What goes into the landfills cannot be controlled and the mixture of waste releases toxic agents from the more volatile waste, and gases, most notably methane from the other degradable waste, into the atmosphere which would be difficult to capture it everywhere, which is utilised in the U. K. Total solid waste in the EU is 520 Kg/year per person of which 10%-15% is plastics, more than 50 Kg, of which 40% is sent to landfills [mooney brian p] which is about 10 million tonnes, with the EU population at 0. 5 billion [eurostat].

Recycling polythene carrier bags rather than producing new plastic has many environmental benefits such as:

- Reducing energy consumption by almost 67%
- Produces 33% of sulphur dioxide and 50% of nitrous oxide
- uses almost 90% less water
- Emits almost 250% less carbon dioxide

One of the most important factors that it saves 1. 8 million tonnes of oil for one tonne of polythene recycled. [wasteonline] Not accounting for the total carbon footprint of the process.

But recycling is not very efficient process compared to producing new materials, every time plastic is recycled it loses about 10% of its mass, [green plastics] reducing the mass of the material to 73% of its original after only 3 recycles.

The current proven world crude oil reserves of about a total of 1, 342 billions of barrels[eia. doe. gov, no title], is estimated to run out by 2040[imeche] at current rate of consumption, though there are critics who would oppose these figures, therefore even more urgency in developing sustainable biodegradable polymers by then is required with the population doubling.

### **How they are made?**

Biodegradable polymers can be based on a variety of environmentally sustainable materials, or a combination of different biomass, and also from bacteria. The most basic material that is used is starch which is abundantly available, large quantities present in corn and potatoes but also all vegetables, and at a low price. Cellulose is another commonly and easily accessible material that is being used to produce bioplastics. Certain oil based polymers have a degree of biodegradability too, polymers such as polycarbonate, polyhydroxybutyrate and poly vinyl alcohol [ Brody&Marsh ] or other biomaterials added to make it biodegradable though it may not be possible for the polymer to degrade 100%. Not all biodegradable polymers are derived from biomaterials or oil some can be synthesised, Aliphatic polyesters [ mulch films ].

### **Starch**

Starch molecules are polymers of Glucose molecules, where all the sugars are oriented in the same direction, as shown in the diagram below. Starch is made up of two types of molecules amylose and amylopectin, depending on the type of the plant starch can contain upto 25% amylose and 80% amylopectin [Poon, introduction to organic].

Starch granules diameter are averagely in the range 5-40  $\mu\text{m}$ , depending on the source, they are not suitable in the plastic industry as they are difficult to process during extrusion and injection moulding. Starch therefore has to be processed, physically and chemically, before it can be used as thermoplastic starch, TPS, which usually includes heating it up in the presence of water to form a gelatinous material, but may require further treatment as this type of TPS is not moisture resistant [ 36/41. wang ].

To ensure that polymers were degraded in the environment after their service life starch was mixed with a range of polymers, such as polyethylene [ 50 Ke. Ty ], but because these class of polymers contain non-degradable polymers which will not be degraded, and cannot be seen, they cannot be called biodegradable polymers.

Thermoplastics starch are therefore mixed with vinyl alcohol to create composites that tend to be more stable, but reducing the starch content in the thermoplastic polymer composite will reduce the biodegradability of the polymer[37].

TPS mixed with other biodegradable polymers ensure a 100% rate of degradation, which is not the case as mentioned when mixed with other polymers. TPS are mixed with synthetic polymers such as poly-(lactic acids) (PLA), poly(glycolic acids) (PGA) etc. [50, ke. ty]

PLA blended with starch can reduce the costs of the polymer in addition to greatly reducing its rate of degradation, the raw materials of PLA is produced by fermenting carbohydrates from renewable sources, such as corn [50].

## **Cellulose**

Cellulose is a type of polysaccharide, a carbohydrate, found in plant cell walls and the most abundant organic material on earth, 40% of all organic matter [ green plastics ], it is produced by plants by natural photosynthesis from CO<sub>2</sub> and water, at an annual rate of 200 billion tonnes, of which 6 billion tonnes are used [ 45. simon. J ] .

Cellulose is similar to starch with the main difference being the molecular arrangement, in starch the molecules are highly branched and in cellulose the molecules are linear. Due to the arrangement molecular structure of cellulose, it cannot be processed into a thermoplastic but has to be converted to derivatives e. g esters and ethers to reduce the intermolecular forces for molecular flow to occur under heat and shearing conditions, unlike processing starch it does not require moisture [ thermoplastic starch ] .

Attempts to produce polymers from cellulose, like polymers from starch, during past half a century were discouraged by textbooks expressing that because cellulose has a rigid backbone it cannot be converted to a polymeric material [ 54. yoshioka].

The figure shows various polymer derivatives from starch and cellulose, with the hydrogen in the starch molecules replaced by the R groups to form different polymers [ 14. second grn rev ]. Nitrocellulose, a highly explosive material, for instance is produced by reacting cellulose with a nitrating acid, mixture of nitric and sulphuric acids, and with alcohol or a plasticizer, such as camphor to make it more flexible and mouldable, added to stabilise the process [ 40. azom ] .

Cellulose acetate is one of the more important and used cellulose derived biodegradable polymers, usually prepared from high grade cellulose, obtained from fast growing trees or cotton linters [ 53. alexander ]. It is commonly prepared by synthesising raw cellulose acetic acid followed by acetic anhydride in the presence of sulphuric acid, which acts as a catalyst, producing primary cellulose acetate, known as cellulose triacetate. The triacetate can then be formed into a solution, using methylene chloride as a solvent, which can then be dry-spun to form fibres, to produce cellulose diacetate. Finally cellulose diacetate can be dissolved, acetone as a solvent, to form fibres known as cellulose acetate [ britannica ]. All three groups of cellulose acetate are similar, what differentiates them is the percentage of hydroxyl groups that are acetylated, according to the Federal Trade Commission, of America, 92% of hydroxyl groups must have acetylated to refer it as a cellulose acetate, else the generally referred to it as cellulose triacetate [ 52. rules® ] .

To produce a process-able polymer the cellulose acetate particles is mixed with a liquid additive, mixing thoroughly using a high speed mixer resulting into fine grained powder and extruded to form granules. Processing parameters that apply are 20-30D screw-type mixer, temperature range 160-190 °C and pre-drying for 2 hours at 70°C. These granules can then be subjected to standard thermoplastic processing techniques [ 53. alexander ].

Lignin is another second most abundant component of woody plants, 20% of all organic material [green plastics], which is not yet used to its full potential, small amount used in various industries. There are new methods being developed to produce lignocellulosic biomass.

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## **Proteins**

There is not a huge amount of information available on biodegradable polymers derived from proteins. One reason may be that plants do not contain a high amount of proteins to be efficient enough to produce polymers, such as 100 grams of corn contains only 3.22 grams of proteins but 19.02 grams of carbohydrates, almost 6 times as much. Soybean the highest protein containing 36 grams of protein and almost as much carbohydrates, but yielding only 50% of the crop per unit area when compared to maize [ 61. lobell ].

Protein just like starch and cellulose can be regarded as a polymer made up of chains of various amino acids. Proteins from various crops have been used to produce polymers, especially zein and gluten, produced in maize and wheat respectively. Zein-gluten composite polymer can be produced by having wheat gluten coated with zein, [ 62. kim, sanghoon ] . The process does not require extrusion processes or high temperature, but only requires of zein to be purified. Kim Sanghoon describes a relatively simple method of producing a protein based biodegradable polymer, from gluten, zein, ethanol and distilled water, and compressed in an aluminium mould.

Other methods of producing protein based polymers include using wood fibres mixed with gluten is plasticized using glycerol, water and ethanol, and extrusion moulded,[ 65. Wu. Qiangxian ] unlike the Sanghoon method.

Sources of proteins used to produce biodegradable polymers include feather-meal, waste animal proteins [60. feathermeal], soy bean [ 58. nanda], egg white [ 39. Egg white ].

## **Synthetic Biodegradable Polymers**

Biodegradable polymers can be synthesised in lab, but because the costs involved the materials are further mixed with a natural polymer, usually starch, as it is abundant and cheaply available or a cellulose derived polymer.

A few of the synthetic biodegradable polymers to name are polyglycolide (PGA), polylactides (PLA) (also known as Poly (lactic acid)), polyhydroxyalkanoate (PHA).

Synthetic polymers can generally offer greater advantages compared to naturally derived polymer, as they can be engineered to have the desirable properties, and have more consistency, unlike naturally derived polymers they do not depend on the source of the raw material which can influence the properties and quality of the final polymer.

Aliphatic polyesters are the most widely and commercially used synthetic polymers available, a few are named above, other polymers that have emerged in the market are polyester containing aromatic moieties. The synthetic biodegradable polymers may be classified into three groups, but the literature will only review polyesters

1. Polyesters
2. Polymers containing both esters and other heteroatom-containing linkages in the main chains
3. Polymers with heteroatom-containing linkages other than ester linkages in the main chain

Biodegradable polyesters can be synthesised in a number of ways

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1. Polycondensation reaction diols and dicarboxylic acids
2. Self-polycondensation of hydroxyacids
3. Ring opening polymerisation

Of the above three processes polycondensation, also known as step-growth polymerisation, and ring opening polymerisation are more widely. Some polyesters synthesised by polycondensation are Poly (lactic acid), Poly (glycolic acid), Polycaprolactone. The process involves the monomers of the two raw material reacting to progressively form long chain polymers, as the secondary name suggests. One disadvantage of the process is that the water production from the reaction must be continuously removed, leading to lengthy reaction times and producing varying chain length polymers.

[ reviewed by 75. RaySmith/& 73. Okada ]

Poly (lactic acid), a linear aliphatic polyester, based on lactic acid, which can be produced by fermenting carbohydrates or by chemical method. Lactic acid contains both the hydroxyl and carboxyl groups needed for polycondensation, but requires removal of water, by azeotropic distillation, as mentioned, to avoid poor yield, further production methods of various aliphatic polyesters is provided M. Bhattacharya.[ by Bhattacharya p337 in 75. RaySmith ]

Ring opening polymerisation is a form of addition polymerisation, where cyclic monomers join a reactive centre (terminal end of a polymer), a range of anionic, cationic and coordinative initiators/catalyst are mentioned in scientific literature, to form long chain polymers through ionic propagation. [R Jerome p77 reviewed by 75. RaySmith]. Ring opening polymerisation is advantageous than polycondensation such that it takes place in milder

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reaction conditions and there are no side reactions, giving a more controlled end product [ 73. okada ], one of the most used polymers in the market Nylon 6 is produced using this process.

The ring-opening polymerisation can be initiated by many organometallic derivatives of metals such as Al, Sn, Y, Nd, Yb, Sm etc, which have d-orbitals of favourable energy, metal alkoxides, e. g. aluminium alkoxides, tin alkoxides, may acts as typical initiators.

Polyhydroxyalkanoates (PHA) are a class of biodegradable polymer, polyesters , produced by using bacteria, e. g. Pseudomonas, Bacillus, Ralstonia etc, especially members of the Halobacteriaceae, as the production centre. The PHA is synthesised within the bacteria that functions as an energy storing water-insoluble compound in the cytoplasm of the bacteria cell[80. anderson]. Bacteria that do not produce PHA can be modified to produce them, e. g. cloning PHA operon, nucleotide sequences of DNA that control the production of PHA, into E. Coli bacteria allows the production of PHA by the bacteria. PHA are then produced by the bacteria when it supplied with source of high carbon content, like glucose under nutrient-limiting conditions. The described way producing is considerably more expensive than oil based polymers there have been suggestions of using products from the food industry as a feedstock for the bacteria to produce PHA, malt waste from a brewery is one of the suggestions, where bacteria produced upto 70% polymer, of dry cell weight (DCW). [82. Yu. Peter]

Recent research groups have been forced to find alternate methods of producing PHA, due to the costs involved in the conventional method, and

have been experimenting successfully with transgenic plants, where the only raw materials required would be CO<sub>2</sub>, for carbon, and sunlight. Other areas that have attracted research to produce polymers of the PHA family are the cyanobacteria, that produce the P(3HB) by oxygenic photosynthesis, but their yield rates are very small compared to the conventional method.

*Synechococcus* MA19, a unicellular thermophile, can store up to 55% DCW.

[reviewed by 78. philip]

### **Rubber**

Rubber is an elastomer and a polymer of isoprene, it can be synthesised or be derived from the Brazilian rubber tree, *Hevea Brasiliensis*, from which most natural rubber is derived, but unlike the name suggest, over 95% of natural rubber in 2008 was produced in Asia, mostly south Asia, but synthetic rubber still makes a greater portion of the market, 56% of the world supplied with synthetic rubber.

Rubber like material was developed based on thermal polymerization epoxidized soybean oil (ESO) with triethylene glycol diamine (TGD), which produce a polymer behaving as a rubber-like elastomer [reviewd in 107. soybean].

Another method to produce natural rubber is by using PHA, which is obtained from bacteria as described, which will therefore be completely biodegradable. The PHA surface is however hydrophobic making it difficult for the microorganisms to inhabit on the surface and degrade, hence its increasing its shelf life significantly, but still be degradable in a composting environment. [109. rubber bacteria]

### **Properties and Enhancements**

The most important property for all biodegradable polymers, or degradable polymers, is that they are completely degradable into basic components, CO<sub>2</sub> & CH<sub>4</sub> and H<sub>2</sub>O, including any other organic compound, by the means of microbial attack, or any other naturally occurring process for the polymers that are classified as degradable by other means.

Properties of biodegradable material should be separated into three categories, the naturally derived polymers, synthetic polymers and the composite of these polymers.

### **Naturally Derived polymers**

TPS shows excellent degradability and composting ability in the soil, partly due to the water solubility of starch. It also has a good oxygen barrier and is not electrostatically chargeable [ 7. Lorcks ].

Unmodified starch polymer have poor processability and mechanical properties, compared to the other polymers available, but plasticising the starch, by addition of water, can assist in processing of the starch, and treating it at a certain temperature would transform the starch into TPS, which show thermoplastic behaviour and properties. As seen in Figure the pure form of TPS has the least period of degradation, but treating it with other biodegradable polymer to enhance its properties increases the time it takes to completely degrade.

Cellulose is water-insoluble and like starch fully degradable, and composed of D-glycopyranoside units, but unlike starch, linked by  $\alpha$ -(1-4) bonds, it is linked by  $\beta$ -(1-4) bonds. The molecular arrangement of cellulose, explained

previously, and the bond type contributes to the longer periods it takes to degrade, which is transferred to the polymer it is based on. Cellulose will readily decompose on heating, therefore cannot be heated to process, but is synthesised into cellulose acetate which like starch shows properties and characteristics of a thermoplastic, but the time it takes to degrade is reduced as the cellulose content of the polymer is reduced.

Cellulose and starch the two of most used and abundant organic compounds having similar properties, except the time to full degradation, both have the characteristic of their glass transition temperature and melting temperature being close to their decomposition temperature.

M. Gaspar [83. reduce water absorption] conducted experiments to examine and improve water absorption in starch based polymers. The experiment contains four specimens of TPS, TPS w/Cellulose, TPS w/hemicelluloses, TPS/polycaprolactone and TPS w/zein each composite having the same proportion, by weight, of the additive. The results showed that TPS w/zein had the highest tensile strength & Young's modulus and TPS w/cellulose the lowest tensile strength and TPS w/polycaprolactone the lowest Young's modulus.

The table shows a few of the mechanical properties of the polymers described above, noting that the 2 different types of starch have significantly differently poreprties.

Film type	Test condition	Tensile strength	Elongation at break (%)	Water vapor permeability
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		(MPa)		(gmm/m <sup>2</sup> daykPa)
Cassava starch	25°C 75% RH	9. 0-17. 0	9. 0-28. 0	
Corn starch	25°C 75% RH	3. 8-4. 3	4. 0-10. 0	
Low density polyethylene	38°C 90% RH	7. 6-17. 3	500. 0	0. 08
High density polyethylene	38°C 90% RH	17. 3-34. 6	300. 0	0. 02
Cellulose acetate	38°C 90% RH	48. 5-82. 7	15. 0-45. 0	
Polyester	38°C 90% RH	178. 0	70. 0-100. 0	
Cellophane	38°C 90/0% RH			7. 27

PLA is a synthetic biodegradable polymer, that is brittle and has poor impact strength, leading to failure of the material by cracking and tearing, and therefore preventing a more widespread use of the polymer in the packaging industry.



Another PLA property is its natural yellow tint, which again is a factor that prevents it uses in the packaging industry, which leads to poor presentation of a consumer product.

PLA is therefore blended with other biodegradable polymers (to keep it 100% biodegradable) to improve the properties that are most desirable. Usually is PLA mixed with plasticizers such as pole- $\epsilon$ -caprolactone, poly (vinyl acetate), starch, poly(hydroxyl butyrate), providing the PLA with more ductility, but having a negative effect on the tensile strength[91 to 99]. The brittleness of PLA can be counter acted by mixing it with a plasticiser, which also reduces the already low glass transition temperature further reducing its end product applications.[100 & 101]

F. Byrne [90] tested PLA mixed various available masterbatches, commercially available polymer additives, to check the enhancements, and the results are as in table, of them all PLA dcS511-Ice clear appears to be the best option for an additive as it removes the tint from the material.

Table Thermal, mechanical, optical and surface properties of PLA and PLA/masterbatch blends

Properties determined	Units	PLA	Biomax Strong	PLA dcS511	PLA dcS515-N	PLA dcS511-Ice clear
Glass transition temperature	oC	59	59	59	58	58
Melting temperature	oC	150	150	151	150	151

Crystallinity	%	90	57	45	74	40
Tensile strength	MPa	68	66	67	66	64
Tensile modulus	MPa	2.3	2.0	1.9	2.0	2.1
Impact strength	N	90	390	90	90	90
Shore D hardness		69D	59D	64D	69D	64D
Haze	%	19.5	67.9	20.6	13.5	10.9
Yellowness index		7.2	10.0	5.8	10.8	0

Another method of improving the properties of polymers is by producing polymers, an example can be of PLA matrix with natural fibres which may include plasticizers, but still remain completely biodegradable. An experiment included using polypropylene (PP) and PLA matrix, including PLA with plasticizer, with flax fibres. The pure PLA had better mechanical properties than the pure PP, and reduced tensile strength as composites. The results showed the PLA with 30 wt.% flax fibre are a 50% stronger than similar composites made from PP, another study [104 sisal] used sisal fibre in a PLA/Starch composite but resulted in poor mechanical properties.

PLA/triacetin, plasticizer, composite with flax fibre reduced the strength of the composite but made it more ductile, effect of the plastizer.

PP/flax fibre of 30 wt.% are commonly used in industrial applications that has an elongation to break of 2.7% with a tensile strength of 29MPa, even though fibres greatly increased the PLA strength its ductility was reduced to successfully replace the PP composite a suitable fibre could be researched or PLA/15wt.%Triacetin with elongation to break 2.6% and tensile strength 37.2MPa could be used. When using natural fibres in a polymer matrix composite the inconsistency of natural fibres length and properties must be considered, therefore using synthetic biodegradable fibres, cellulosic origins, an even quality can be obtained[105. herrmann].

### **Degradation**

Oil based plastics are resistant to biodegradation, and most other forms of degradation, as the micro organisms responsible for the degradation of these polymers are unable to consume it, mainly due the impenetrable oil based matrix which are they are made from and the surface in contact with the soil is smooth [reviewed in 113 p, p, future] . Another class of polymers are the partially degradable are oil based polymers composites with a easily degradable fibre, e. g. starch, which breakdown as the microorganisms attack the starch and leave the oil based polymer particles behind, which degrade at a much slower rate, but unnoticeable because of the size. Complete degradation of a material occurs through various mechanisms, by microorganisms, light, water etc. Biodegradation can be generally be classified into two categories aerobic and anaerobic biodegradation, where the final products of each of the degradation are CO<sub>2</sub>, H<sub>2</sub>O and biomass of aerobic and CO<sub>2</sub>, CH<sub>4</sub> and biomass of anaerobic.

CPolymer + O<sub>2</sub> → CO<sub>2</sub> + H<sub>2</sub>O + CResidue + C Based biomass

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Generally in plastics the amorphous region is more vulnerable to degradation by hydrolysis, as water is easily penetrated into this region. The degradation can be classified into surface degradation and bulk degradation, where surface degradation occurs when the degrading agents are not able to penetrate into the bulk layer of the material and act only on the material surface. Spherulites may be visible on the material undergoing surface degradation.

It must be noted that materials in the environment may not be degraded by one specific mode of degradation but a combination of different mechanisms, so it would be sensible to consider degradation of a polymer in the soil to have two mechanisms of degradation acting on it, biodegradation and hydrolytic degradation, and photo-degradation if it is exposed to sunlight.

Degradation can be considered to occur in two phases, disintegration and mineralization. The disintegration of polymers may occur through hydrolytic degradation, photo-degradation or thermal-degradation by exoenzymes, mediated or not [114. scott]. The hydrolytic degradation is most likely to occur and have a greater role in the process of the biodegradation of the polymer, the figure below shows the subdivisions of hydrolysis. The mineralization takes place when the microorganisms start to metabolize the disintegrated polymer particles and convert them to common inherent digestion products [6 Krzan].

Natural rubber exists in the environment the various microorganisms required to metabolise the polymer are already widely distributed in the

environment. The process starts by the oxidation at the double bond of the polymer chain, leading to the formation of carbonyl, peroxide or epoxide groups. The microorganisms secrete a rubber degrading extracellular enzyme, which in a sense start a chain reaction, as lower-molecular weight fractions are further metabolised by the microorganisms.

An industrial scale degradation