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Bioplastics: A Green Alternative To Plastics

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Introduction:

The first known bioplastic, polyhydroxybutyrate (PHB) was discovered in 1926 by a French researcher Maurice Lemoigne from his work with the bacterium Bacillus megaterium. Logo natureplast historically, the very first plastic materials used industrially by man were of natural origin. Before mastering monomers obtained from refining oil, starting from the 1930s, several objects used in daily life were manufactured using biobased polymers. The resources used were natural rubber (discovered in the 18th century), cellulose with Parkesine, celluloid or even cellophane at the end of the 19th century and the beginning of the 20th century or even milk components like casein which resulted in the manufacturing of Galalith in 1897. Decades later in 1947, Rilsan (or Polyamide 11) was the first technical bioplastic introduced on the market, with its excellent mechanical properties and chemical resistance. It was then followed in the 1990s by bioplastics which are well-known today, PLA, PHAs, or even plasticized starches which benefited from the rapid technological advances in green chemistry and white chemistry in the recovery of biomass (starches, sugars, cellulose, etc.). In addition to biobased or biodegradable polymers which are created regularly like PEF, the main developments are based on the diversification of the resources used to produce these materials, with the essential part of the work being focused on the reclamation of by-products or waste material from various biomasses.

“Bioplastic” simply refers to plastic made from plant or other biological material such as vegetable fats and oils, corn starch, straw, woodchips, sawdust, recycled food waste etc. instead of petroleum. It is also often called bio-based plastic. The term "biobased" means that the material or product is (partly) derived from biomass (plants). Biomass used for bioplastics stems from e.g. corn, sugarcane or cellulose. Globally, Bioplastic packaging in relation to the production of packaging conventional plastics are being replaced by bioplastics at a rapid rate. There's a big demand for bioplastic packaging and it is the largest segment of the European bioplastic market estimated at around 44% of 2.05 million tonnes in 2017. According to 2013 and 2018 analysis, global production of Bioplastics is drastically increased. The materials used in food packaging based on non-biodegradable synthetic polymers pose a serious threat of pollution to the environment. Hence, research is now focused on developing eco-friendly and biodegradable packaging obtained from natural polymers.

Biodegradable: Biodegradation is a chemical process during which micro-organisms that are available in the environment convert materials into natural substances such as water, CO2, and compost (artificial additives are not needed). The process of biodegradation depends on the surrounding environmental conditions (e.g. location or temperature) on the material and on the application. They are biodegradable i.e., the material returns to its natural state when buried in the ground. These are naturally degraded by the action of microorganisms such as bacteria, fungi, and algae. These are produced from renewable resources and degradable materials mean which can reduce pollution.

Reasons for developing/using bioplastics:

The expansion and development of the Bioplastics and their products would lead to an increase in the sustainability of the environment, reduces the use of fossil fuels and greenhouse gas emissions. The development of sophisticated bioplastic packaging for food products has greatly improved the shelf life of the food and often it allows a significant reduction in the carbon footprint and shows the good performance levels of biobased polymers in terms of greenhouse gas emissions and fossil fuel savings.

Bioplastics provide an alternative approach to packaging and are a real solution to the need for a reduction in conventional plastic use and waste. Plant-based polymers are able to fully compost at the end of their useful life. It's relatively easy for manufacturers to produce bioplastic packaging because packaging made from biopolymers can usually be produced using standard plastics processing technology so no special equipment is needed. There's everything to gain and no real downside in this context so this switch to bioplastic packaging is set to impact all our day-to-day lives for the better.

The Bioplastics innovation would be key to the long term solution for plastic pollution. However, widespread public awareness is also essential in effecting longer-term change against plastic pollution. Developing these materials has allowed for the creation of new pathways in the fields of Agriculture, chemistry and keeping with the approach of sustainable management of our resources.

Types of bioplastics

Bioplastics are majorly divided into 3 types. They are

1.Natural polymers/Polymers derived from biomass.

2.Synthetic polymers/Polymers chemically synthesized from renewable sources.

3.Microbial polymers/Polymers derived from microorganisms.

Based on origin these polymers are classified into different ways.

- **Natural polymers/polymers derived from biomass**

The natural polymers are derived from animal, marine, and agricultural sources, which include the polysaccharides such as starch, cellulose, chitosan, gums etc. Plant-derived proteins like zein, gluten, soy etc. and animal extracted proteins like casein, collagen, gelatine etc. and lipids including cross linked triglycerides. By nature, most of these Polymers are hydrophilic and crystalline in nature. They have excellent gas barrier properties which make them acceptable for their utilization in food packaging.

- **Starch**

Starch is the most abundant commonly used renewable material and easy raw biodegradable natural resource. It is obtained from seeds, corn, wheat, rice, potato, sweet potato, and cassava. is usually used as a thermoplastic and constitutes a substitute for polystyrene (PS). It is plasticized through destructuration in presence of specific amounts of water or plasticizers (glycerol, sorbitol) and heat, and then it is extruded. Starch is an attractive material for packaging applications because of its relatively low cost, and

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biodegradability. Pure starch is able to absorb humidity because of this property these are used in the production of drug capsules in the pharmaceutical sector. It is sensitive to moisture and has high water vapour permeability.

- **Cellulose**

Cellulose is the most abundant natural polymer and is derived by a delignification from wood pulp or cotton linters. Cellulose is a very inexpensive natural resource. It is soluble in hydrogen bond breaking solvents such as N-methylmorpholine N-oxide. Cellulose can become thermoplastic when extensively modified. An example of this is cellulose acetate. Cellulose have high transparency, high impact, mechanical strength, aesthetic appeal and excellent machine-ability. It has good resistance to a variety of chemicals. Cellulose is very difficult to use in packaging because it is hydrophilic and crystalline in nature possessing poor mechanical properties in its raw form. Therefore, it must be treated with chemicals like NaOH, H2SO4, CS2, etc. to produce cellophane having excellent mechanical characteristics.

- **Chitosan or chitin**

Chitosan or chitin is the second abundant polysaccharide resource after cellulose found in nature. It has antibacterial and antifungal activities. Chitosan has the ability to absorb energy from metal ions. It has good water-retaining and moisturizing properties. It naturally appears in the exoskeleton of arthropods and in the cell walls of yeasts and fungi. It is produced commercially by chemical extraction processes from prawns and crabs wastes. Chitosan is obtained from the deacetylation of chitin, and different factors (e.g. alkali concentration, incubation time). Chitosan forms good films without the addition of additives, exhibits good carbon dioxide and Oxygen permeability, as well as excellent mechanical and chemical properties which reduce the oxidation process and is beneficial for increasing the shelf life and quality of food products.

- **Proteins**

Proteins are complex structures made up of amino acids and can be obtained from plants like wheat gluten, corn, zein, soy protein etc., and animals like casein, whey, keratin, gelatin, etc. sources. They are highly desirable for packaging materials due to the presence of a unique sidechain in their structure. Due to the renewable nature, biodegradability and excellent gas barrier properties proteins and protein-based materials are used in many industrial applications.

- **Casein**

Casein is a milk-derived protein, when processed with suitable plasticizers at a temperature of 80°C-100°C, form materials with mechanical performance varying from stiff and brittle to flexible and tough performance. It has excellent barrier property. Casein films have an opaque appearance. Irrespective of its relatively high price, it is used today for bottle labeling because of its excellent adhesive properties. It dissolves in water.

- **Gluten**

Wheat Gluten plastics exhibit high gloss and show good moisture resistance under certain conditions. These are the homogeneous, good translucent and excellent gas barrier. It is mechanically strong. They do not dissolve in water but absorb some water on immersion.

- **Soy protein**

Soy proteins are flexible, smooth and transparent. It has excellent mechanical property and slight water resistance. It is commercially available as soy flour, soy concentrate and soy isolate. Soy protein isolate (SPI) may be used to prepare edible and biodegradable packaging films. The films obtained from SPI exhibit excessive friability.

- **Keratin**

The cheapest protein, keratin extracted from waste streams such as hair, nails and feathers. It increases flexibility. It contains high tensile strength, high resistance to water and tearing. Keratin the most difficult protein to process due to its structure and a high content of cysteine groups.

- **Synthetic polymers or chemically synthesized from renewable sources**

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They are produced from classical chemical synthesis from biobased monomers. In this category, polylactic acid (PLA) is one of the most commercially available and exploited bioplastics.

- **Polylactic acid (PLA)**

PLA is one of the most promising and biodegradable polyesters made from renewable resources such as corn, sugar beets, and potato starch for commercial use as a substitute for high-density polyethylene (HDPE) and low-density polyethylene (LDPE), polystyrene (PS) and polyethylene terephthalate (PET). It is obtained by conversion of corn, or other carbohydrate sources, into dextrose, followed by fermentation into lactic acid. Through direct polycondensation of lactic acid monomers or through ring-opening polymerization of lactide, PLA pellets are obtained. The processing possibilities of this transparent material are very vast. ranging from injection molding and extrusion over cast film extrusion to blow molding and thermoforming. PLA is becoming an advancing alternative as a green food packaging material because it was found that in many circumstances its performance was better than synthetic plastic materials. PLA comes in the form of films, thermo-formed cups and trays, containers and coatings for paper and paper boards.

- **Microbial polymers/polymers derived from microorganisms**

This class includes the polymers that are synthesized from the microbial fermentation of polysaccharides. It is a quite recent and innovative field that has immense potential in industry. This category includes the polymers, such as poly hydroxyl alkanoates (PHA), poly hydroxyl butyrate (PHB), etc. and microbial polysaccharides like pullulan, curdian and xanthan.

- **Polyhydroxyalkanoates (PHAs)**

The polyhydroxyalkanoates (PHAs) are biodegradable, thermoplastic, biocompatible and thermo stable having a melting temperature of about 180°C. These polymers are produced in nature via bacterial fermentation of plant-derived feedstock’s such as sugars or lipids and then harvested by using solvents such as chloroform, methylene chloride or propylene chloride. These polymers are alone or in combination with starch or synthetic plastic give excellent packaging films, among more than 100 PHAs composites, PHB is the most common type of PHA, coming from the polymerization of 3hydroxybutyrate monomer with properties similar to PP but stiffer and brittle. It degrades under both aerobic and anaerobic conditions forming CO2 and H2O. Besides being insoluble to water, PHB is optically active and has good barrier properties toward gas. The PHAs have potential as an alternative for many conventional polymers, since they possess similar chemical and physical properties. PHAs also exhibit printability, flavour and odour barrier. Heat sealability, grease and oil resistance, temperature stability, and are easy to dye which improves its applications in the food industry. The utilization of several microbial polysaccharides, such as xanthan, pullulan and curdlan etc. as a packaging film is a novel concept and needs biotechnological techniques.

- **Pullulan**

Pullulan is produced by yeast-like fungus Aureobasidium pullulans. It is a linear, water-soluble, non-toxic, nonmagnetic edible biopolymer with excellent film-forming abilities and adhesive properties. It is employed for packaging in several industries like food. medicine, and cosmetics. Pullulan based films homogeneous, transparent, printable, heat sealable, and flexible. It act as good barrier to oxygen, tasteless, odourless, non-toxic and biodegradable in nature. Pullulan membranes inhibit fungal growth thus making them suitable for food applications.

- **Curdlan**

Curdlan, the bacterial polysaccharide, is produced from Agrobacterium bio bar and Agrobacterium tumefaciens and is mainly used as a gelling agent in the food industry enormous potential in the development of packaging films, which is yet to be discovered.

Mechanism of Biodegradation

Biodegradation means disintegration, or loss of mechanical attributes of packaging materials using microorganisms and is preceded by hydrolysis followed by Oxidation. The rate of biodegradation depends on temperature (varying from 50 to 70°C) humidity and kind and amount of microorganisms. In industrial composting bioplastics are converted into water,

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CO_2 and biomass in about 6-12 weeks. The degradation can be aerobic or anaerobic in nature resulting in the formation compost or sludge in the former case and methane and hydrogen (biogas) and in the latter. Natural biopolymers like starch, cellulose, etc. are hydrophilic and swellable in nature in contrast to the polyolefins that are used in central packaging material and are hydrophobic in nature, exhibiting high resistance toward hydrolysis, peroxidation and biodegradability. Prooxidants must be incorporated in polyolefins to initiate the oxobiodegradation in them. The oxobiodegradation mechanism is followed in the biodegradation of synthetic and natural polymers however, standard biodegradation requires the instant mineralization measure.

Further, oxobiodegradation at room temperature is a very slow mechanism as compared to hydro biodegradation. The oxobiodegradation of carboxylic acid (COOH) results in alcohol, aldehyde and ketone molecules, which are degradable using low molar mass generated during the peroxidation that is initiated either by light or heat. This is the main reason the hydrocarbon polymers lose their mechanical properties. After this, bio assimilation starts by the fungal enzymes or bacteria, giving rise to CO_2 and biomass that finally produce humus. Generally, synthetic polymers contain antioxidants and stabilizers are added to inhibit the oxidation of polymers during biodegradation process and to increase the shelf-life of materials and to improve the performance also. Biodegradation nature offers an additional option for the end of life of the product and allows for a reduction in the amount of water.

Comparison between plastics and bioplastics

Biodegradable Plastics (BPs) are made of organic (plant material) while SPs (normal plastics) are made with chemical filters. other major difference is: on decomposition SPs released GHG emissions, while BPs release relatively less or no emissions. BPs can reduce~42% carbon footprints compared with SPs.

Daily uses of bioplastics in our daily life:

It uses expanding in various sectors.

1. Bioplastics disposable items such as packaging, crockery, cutlery, pots, bowls, straws, plates, clingfilm and food containers.

2. Uses of Bioplastics in Agricultural sector such as Agricultural foils, horticultural products, nursery products.

3. Also uses in toys manufacturing, textile industry, houseware and kitchenware, Medical equipment, electronics and Automobile industry etc.

Applications of bioplastics in our everyday life

In these packaging take up a significant share of the Bioplastic market, their usage in other industries has been grow.

Major advantages of bioplastics:

1.Reduces the use of fossil fuels and greenhouse gas emissions

2.The capability to improve the environmental impact of the product

3.Reduced CO2 emission

4.They reduce waste and carbon footprint

5.Their production reduces non-biodegradable waste that contaminates the environment.

6.They do not contain additives that are harmful to health

7.They do not change the flavour or scent of the food

8.They providing energy savings in production

9.Cheaper alternative

10.Multiple end of life options

11.Possibility of using a local resource

12.Reclamation of by products

13. Consumes less energy for manufacturing and provides an eco-friendly solution

Drawbacks of bioplastics:

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The bioplastics are associated with several major drawbacks limiting their use in the industry. Thermal instability, brittleness, low melt strength, high water vapour and oxygen permeability and poor heat sealability etc. hinder the commercial use of bioplastics as food packaging. Therefore, great efforts are being taken to improve the functionality of biopolymers.

Methods for overcoming bioplastic drawbacks coating:

Coating consists of covering of biopolymer using an additional thin film of another material. Several bio-based and non-biobased materials can be used as a coating. For example, PLA can be layered using PCL-Si/SiOx, PEO-Si/SiOx (polyethylene oxide) or PLA-Si/SiOx, which improves the barrier properties of PLA which makes the PLA films suitable for packaging material.

Blending

The blending of two or more biopolymers shows great significance. When we blend materials, compatibility becomes a major challenge. The compatibility for immiscible polymers can be increased by introducing a reactive functional chemical modification or group etherification.

Testing procedures:

Anaerobic biodegradability:

The ASTM D5511-12 and ASTM D5526-12 are testing methods that comply with international standards such as the ISO DIS 15985 for the biodegradability of plastic.

Aerobic biodegradability-ASTM D5338 – 15:

Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, Incorporating Thermophilic temperatures. This test method determines the degree and rate of aerobic biodegradation of plastic materials on exposure to a controlled-composting environment under laboratory conditions, at thermophilic temperatures. This test method is designed to yield reproducible and repeatable test results under controlled conditions that resemble composting conditions, where thermophilic temperatures are achieved. The test substances are exposed to an inoculum that is derived from compost from municipal solid waste. The aerobic composting takes place in an environment where temperature, aeration and humidity are closely monitored and controlled. This test method is designed to yield a percentage of conversion of carbon in the sample to carbon dioxide. The rate of biodegradation is monitored as well.

Conclusion and Future Trend:

In conclusion, using vegetable sourced bioplastics as a replacement for fossil sourced Polymers often allows for a significant reduction in the carbon footprint of the products depending on the applications. Bioplastics can greatly reduce our dependence on fossil resources which are significantly more harmful to the environment. So it's no surprise that you can expect to see a surge in the production and use of Bioplastics in the coming years. Comprehensive research is needed to improve the barriers properties and to maintain the food integrity. Further research and development in biodegradable polymers is the need of the hour because of human responsibility towards environment. That is the main driving force implementing the tremendous potential of biopolymers in the future.

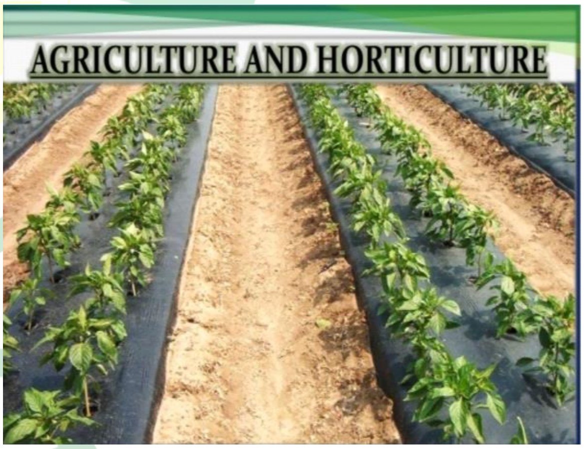

Fig 1. Bioplastics disposable items **Fig 2.** Bioplastics Agricultural foils

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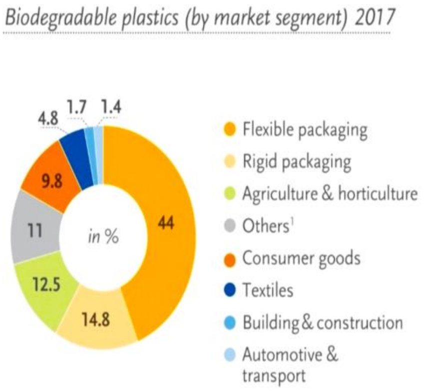

Fig 3. Biodegradable plastics (by market segment) 2017

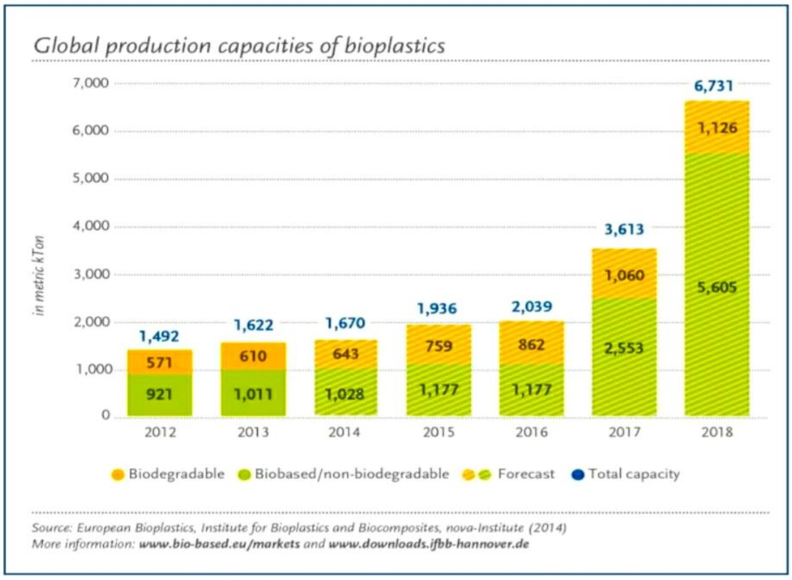

Fig 4. Global production capacity of bioplastics 2018