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EDITORIAL

Plastics came as very useful material to humanity a little more than a century ago. Many varieties of plastics were invented and used. Today, they are ubiquitous and synonymous with human civilization. Plastic manufacturers even claim that they are reducing our dependence on natural resources like trees, hence contributing to ecology of the planet!

The reality is different. Almost all major sewerage lines of any city or town have discarded plastic pieces – mostly carry bags and plastic bottles – choking them. Drains overflow with such plastic waste. Picnic spots are littered with thermocol plates, plastic cups and bottles, and carry bags.

When these drains are cleared, the plastic items do not disappear. They go and accumulate in the seas and oceans. It is estimated that the entire plastic content of our oceans would cover the largest continent in size. Almost everyday, we find carcass of large marine animals are washed ashore, with their entrails choked with plastic. Scientists say that by 2050, there would be more plastic than fishes in the oceans. Microplastics only make it worse.

A few decades ago, a campaign was initiated in our country to “avoid single use plastics”. People were urged to carry own bags to shops and markets. Shopkeepers were warned and fined if found to deliver goods in single use plastic bags. However, that attempt died a natural death. And the pandemic from 2020 ensured a manifold increase in plastic waste in and around all human settlements.

In this context, the articles on Green Chemistry and Bio-plastics that appear in this issue become important. While Bio-plastics are either biologically modified plastics or plastics that degrade in the environment like biomolecules, Green Chemistry is an alternate way of doing chemistry, that not only is environment friendly, but also use less resource.

We hope the articles generate interest among people, especially youngsters, regarding these topics.

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Green Chemistry and the Environment

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1. Introduction

Before we discuss Green Chemistry, we must ascertain why it is necessary to discuss it. This is because traditional chemical knowledge, which gave us ~4 trillion US\$ business (approx. current figure) called global chemical industry, besides important offshoots such as global pharmaceutical industry (405.52 billion US\$ in 2020 and estimated to grow at over 11% rate till 2028) and cosmetics industry (~400 billion US\$ and growing), have had a terrible effect on the environment. The motto of all industries till about mid-20th century was 'dump the waste anywhere'. There was little understanding or appreciation of what this wrought on the environment. Since then, people have become more aware and sensitive to this issue, and there have been laws in all countries about controlling environmental pollution.

Now let us talk about Green Chemistry. It is a way of practicing chemistry which is environment friendly, causes minimum harm or damage to the ecology, and is also efficient and cost-effective at the same time. Without the last two qualities, global finance or business heads would never even consider this subject at all. At the same time, the chemical processes must generate minimum waste and be risk free. It should also not consume too much energy or resources.

2. Commandments of the Green chemistry

Paul T. Anastas, a pioneer of Green Chemistry, laid down his twelve commandments of the topic. These are as follows.

i) Prevention of waste: It is better to have a process which does not generate waste, than to clean up or treat the waste afterwards.

ii) Atom economy: Synthetic strategy should be such that all the starting materials are used or incorporated in the final product. In other words, there should not be atoms or moieties which have minimal role in the reaction.

iii) Hazard minimization: Chemical processes should be such that little or no material is used or produced that can harm or endanger lifeforms or the environment.

iv) Design safer chemicals: Chemical products should be designed to carry out desired functions with minimum or no toxicity.

v) Use safer solvents and auxiliaries: Use of solvents and auxiliary substances should be prevented or minimized. If that is not possible, one should use as much safer solvents and auxiliary substances as possible.

vi) Be energy efficient: Energy requirements for chemical processes must be minimized. If possible ambient conditions (pressure, temperature) must be used.

vii) Use renewables: It is always better to use chemicals that are renewable, rather than costly and rare chemicals, which, once used are thrown down the drain.

viii) Reduce derivatives: Unnecessary derivatization, protection-deprotection etc. increase no. of steps and reduce atom economy. This should be avoided as much as possible.

ix) Use catalysts: Catalytic agents are better than stoichiometric agents, and hence preferable over the latter.

x) Design for degradation: Products should be designed to break down after use and not pollute the environment.

xi) Real time analysis for pollution: Monitoring and control of chemical processes must be carried out continuously to prevent pollution.

xii) Use inherently safer chemistry: Processes must be designed to be inherently safer, without possibility of explosion, fire and other hazards, or causing pollution.

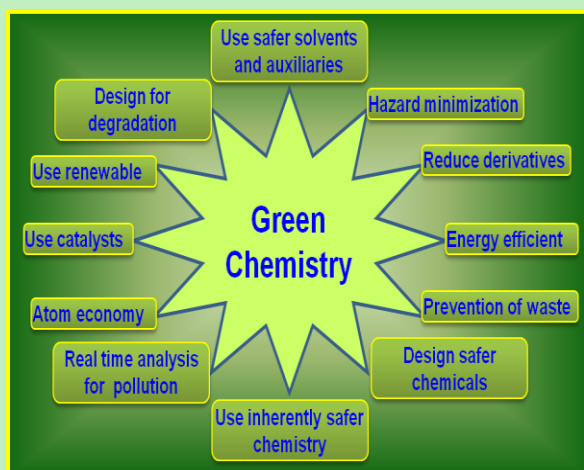
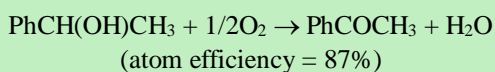
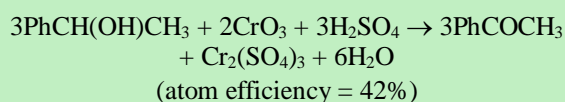


Fig. 1 Branches of Green chemistry

Let us examine some of these conditions in more detail. I do not think there is any need to explain the first principle. As we are all concerned about the health and stability of our environment and that of the planet earth as a whole, we should not do anything to cause damage to this environment. However, the second commandment may be explained further. This means, to use as much of the reactants into the product as possible, without generating unnecessary byproducts or intermediates. Let us consider the following example.



In the first reaction, the conversion is stoichiometric, while in the second, a catalyst was used. Consequently, the second procedure has more of the reactant(s) converted to the product. Hence, atom efficiency is more in the second process. There are many such examples. The atom economy concept was first introduced by Trost. Similarly, regarding less hazardous processes and safer chemicals, there can be no argument. A supreme example of unsafe chemical process was what happened in Bhopal in 1984, when water leaked into a tank containing methyl isocyanate in a Union Carbide plant. In the reaction cited earlier, chromium compound is used in one instance, which can cause great damage to life forms.

As regards safer solvents, water is considered the greenest solvent i.e. the most acceptable. It is also a universal solvent, and supports all life forms. However, there are several chemical reactions which were developed in non-aqueous media such as petroleum ether, chloroform, dichloromethane etc. There has been a lot of research over the last few decades to find alternative ways to carry out these reactions. Apart from water, glycerol, ionic liquids (IL) especially room temperature ionic liquids (RTIL), supercritical carbon dioxide etc. are considered safer solvents to use. However, there are problems with some of these solvents viz. volatility and high vapour pressure. Also, many chemists tend to follow traditional procedures for synthesis or studying reactions.

Energy efficiency need not be stressed much, as we all understand how unit costs of energy can affect prices of all products. This is all the more reason to concentrate on research to find alternate reaction pathways, especially for reagents much in demand, or high value reagents. The same restrictions that apply to chemical processes as outlined above must also hold for activities in this direction. Simple minded solutions such as clearing out large parts of the Amazon rainforest for ethanol production would actually make the overall situation much more toxic and uninhabitable for all of us.

Similarly, use of renewable chemicals has to be taken into consideration. This, and use of catalysts, along with reduction of derivatives, have not been considered in organic synthesis in general, for a long time. There may be some reasons for this reluctance. Perkin's accidental discovery of a method of making aniline dye was a forerunner of the fine chemicals and pharmaceutical industry of latter days. Because of often small amounts of reagents or products involved in reaction steps in these processes, synthetic organic chemists may not have realized the need to seek out new alternatives, and followed traditional routes. Catalysis, on the other hand, was the domain of physical chemistry or materials researchers, who

were more interested in gas phase reactions, and in the underlying physicochemical phenomena. Now, in nanomaterials, we find coming together of various disciplines, and organic and inorganic chemists are involved as much in synthesizing and using nanomaterials as are physical chemists, physicists and materials scientists. Therefore, in recent years, people have been trying to use various catalysts, in reducing number of steps in the reaction, and ultimately, seeking one-pot synthetic steps for designer chemical products. This leads to atom economy, energy efficiency, catalytic instead of stoichiometric procedure, reduction of derivatization, hazard minimization, and often, to safer chemicals and greener processes. Gold, copper, silver and other nanoparticles, quantum dots, doped graphene or graphene oxide composites are some examples of new generation of nanocatalysts which are being taken up by industry.

Use of biological molecules or biomimetics is important in Green Chemistry, as these are used in natural processes. Let us consider a typical example. 6-aminopenicillanic acid (6-APA) is a key reagent for production of many penicillin and cephalosporin derivatives. It is obtained by hydrolysis of penicillin-G. Until about three decades ago, it needed over 20 kg of various materials and stringent reaction conditions (-40 °C for example) to produce 1 kg of 6-APA. It is now produced mostly in water at room temperature in an enzymatic process, with only 0.9 kg ammonia to adjust pH of the reaction, which is a much more green process. There are many more such examples of use of biocatalysts.

The other advantage of using biological ingredients in a chemical reaction is that it may inherently lead to product degradation later. Bioplastics was invented several decades ago, but its use has been limited till date, mainly because of the cost factor. Once the cost of production of these comes further down, we may see a day when plastics do not clog our streams and canals in cities and in the countryside, and are burnt rampantly, especially in winter,

emitting carcinogens and noxious fumes. Biocatalysis is an important area of research today, and we hope industrial processes may be set up to make such products available to all.

Chemistry is a continuously evolving subject. Green Chemistry is still more so. The last principle of Green Chemistry stresses the design aspect of it. Ever since Stewart Warren popularized the disconnection approach, synthesis of chemicals, esp. organic chemicals, involve some design and planning beforehand. Once ideas of Green Chemistry take root in people's minds, we hope that there will be adequate time spent in designing synthetic routes of all chemical products, not only organic chemicals, that take care of the fundamental concerns of Green Chemistry.

Below are some references, where concepts and applications of Green Chemistry have been dealt with in much greater detail. The purpose of the present article will be fulfilled if these are used by active researchers and new, greener routes of some chemical process(es) are found.

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Bioplastics - a new dawn of human civilization

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Keywords: Biobased polymer; Bioplastic; Biodegradability of plastic; Applications of bioplastics.

1. Introduction

The ever growing fossil resource-based 'plastic pollution' in different environmental components is responsible for threatening ecosystems all around the world and endangers health of many categories of biota. Plastic is the third most commonly used petroleum derivative in the world. Each year 200 million tons of plastic are consumed on the planet. These fossil-fuel plastics or petro-based polymers induce toxicity in agricultural field soils, contaminate groundwater and surrounding surface water bodies, and ultimately pose threat to the world food security. The single-use plastic products and microplastics are endangering the eco-fragile environments. In this scenario the invention and use of *bioplastics* is a fresh endeavour towards sustainable future of the human civilization.

Biodegradable plastic materials (Bioplastics), which come from renewable sources, can be used to reduce the problem of plastic waste that is choking the planet and contaminating the environment.

Bioplastics are polymers that are manufactured from biomass resources like vegetable fats and oils, proteins, polysaccharides and starches, corn starch, straw, woodchips, sawdust, recycled food waste etc. (Ashter 2016) as well as from fossil fuel-based resources (Havstad 2020). Many of the bioplastics get naturally biodegraded and thus, they are entirely environment friendly.



Fig. 2 Bioplastic produced from different biowastes

2. Sources of bioplastic

The broad categories of bioplastics are degradable biomass-based bioplastics, non-degradable biomass-based bioplastics and degradable petro-based bioplastics (Endres 2017). Nowadays the main raw materials used for manufacturing bioplastics are seaweeds, hemp, corn waste, shrimp shell, fish scale, walnut shell, chicken feathers, banana peels, vegetable peels, etc.

2.1 Degradable biomass-based bioplastics

This group of bioplastics is manufactured from renewable biomass and is completely biodegradable. They are produced from vegetable oils, sugar, proteins, lignins, polysaccharides (e.g., cellulose) and starches or their chemical/biotechnological derivatives. The polysaccharide-based 'thermoplastic starch' represents approximately 50% of the global biomass-based bioplastics. This is because starch is a widely available cheap and renewable resource (Avérous and Pollet 2014). Cellulose, chitosan and alginate are also used to produce other polysaccharide-based bioplastics. Protein-based bioplastics include plastics made from soy protein, wheat gluten, casein, etc.

2.2 Non-degradable biomass-based bioplastics

These bioplastics are manufactured from biomass although the final products are

sometimes recyclable but, are not biodegradable. Some examples are bio-polyethylene (bio-PE), bio-polypropylene (bio-PP), bio-polyethylene-terephthalate (bio-PET), bio-polytrimethylene terephthalate (bio-PTT) etc. (Rahman and Bhoi 2021). Bio-PE is mainly synthesized from ethanol present in sugar cane, sugar beet, wheat grain, etc sources. Bio-PP, largely used in packaging purpose, is produced from biological resources by butylene dehydration of bio-isobutanol present in glucose, followed by its polymerization. Bio-PETs are prepared from sweet corn, sugar beet, maize grain and orange peels.

2.2 Degradable petro-based bioplastics

The conventional petro-based polymers can be transformed into biodegradable bioplastics by including various heteroatoms (like O, N, etc) in the molecule of the polymers (Endres 2017). For example, polycaprolactone (PCL) and polybutylene-succinate (PBS) undergo microbial degradation (Atiwesh *et al.* 2021). Some other examples of this category of bioplastics are polybutylene adipate-terephthalate, polyvinyl alcohol, oxodegradable plastics, etc.

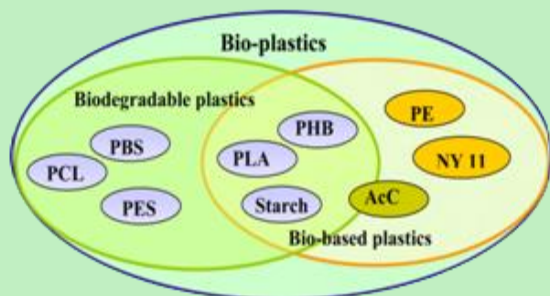


Fig. 3 Biodegradable plastics and Bio-based plastics (Tokiwa *et al.*, 2009).

3. Applications of bioplastic

The different applications of bioplastics include disposable items like packaging, crockery, cutlery, pots, bowls, cups, plates, trays, shopping bags, waste bags, ballpoint pens and straws (Havstad 2020, Lackner 2000). Another important application of bioplastics is as a material for mulching in agricultural fields. They reduce usage of pesticides, control weeds and do not require disposal after cultivation is over.

The use of bioplastics which are biodegradable is beneficial for the environment as it reduces landfill, increases composition of soil composts. These are one of the best alternatives of single-use plastic packaging and catering products.

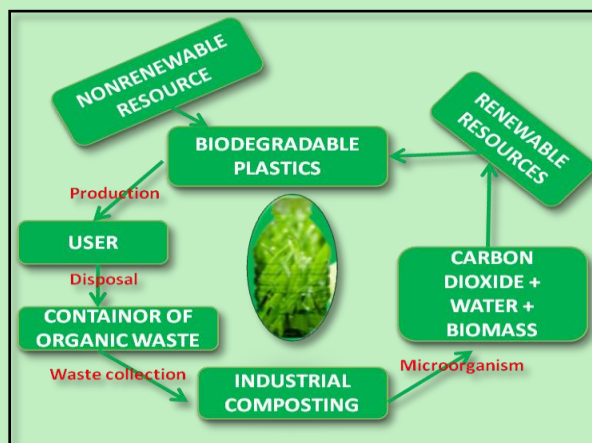


Fig.4 Cycle of biodegradable plastics

Polylactic acid (PLA) is used mainly for the packaging of nonsparkling beverages and dairy products. PLA mostly employs renewable biocarbon and moreover, based on the renewable carbon in the product it provides an intrinsic reduction in the carbon footprint. Polycaprolactone (PCL) products being Food and Drug Administration (FDA) approved are increasingly used in biomedical applications, specifically for long-term implants and controlled drug release applications. Other medical applications of bioplastics include wound sutures and staples, biodegradable screws, pins or plates for pinning and repairing ligaments, polymer tissues, and sponges. The growth of bioplastics industry is expected to grow by 15% from ~2.1 million to 2.4 million tonnes between 2019 and 2024. Bio-PP has major market in automobile sector as ~50% of the plastics used in automobiles are PP. Cellulose ester-based bioplastics are utilized for making synthetic fibers, cigarette filters and formerly photography film (Lackner 2000). Bioplastics have also found their use in biomedical, structural, electrical and other consumer products. Global bioplastics production will more than triple within the next five years

projected by 16th EUBP Conference, Nova-Institute, 2021. (Fig 5).

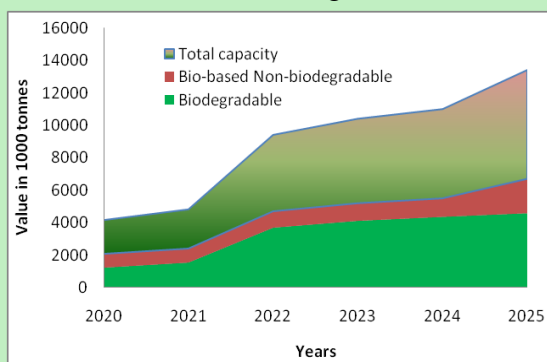


Fig.5 Global production capacities of bioplastic with forecast (Source:European Bioplastics nova-Institute, 2021; www.european-bioplastics.org/market/)

4. Conclusions

The most important property of bioplastics is their biodegradability. They are good alternatives of single-use plastics as well as microplastics (<5 mm). Some of these are stronger and lighter in comparison to conventional fossil fuel-based polymer products. Their use may minimize plastic litters, specifically in eco-fragile tourist destinations. The non-toxic bioplastics are the most suitable for catering products and for packaging of food items. Bioplastics feedstock has a profound potential for creating employment opportunity for rural people. Being based on natural feedstock, production of bioplastics lowers emission of greenhouse gases. Moreover, they give freedom from dependence on crude oil for producing plastics. Biodegradable alternatives of microplastics are alginate, chitosan and gelatin microbeads (Mark et al. 2009).

The term bioplastics is somewhat misleading as all bioplastics are not degradable. The IUPAC has thus suggested using the term as '*biobased polymer*' (Vert et al. 2012). The primary disadvantage of bioplastics is that their high manufacturing cost (Jain and Tiwari 2015). The durability of some bioplastics is very low, as low as a few hours. Hence, they have very limited arena of applications. Bioplastics should not be mixed with standard plastics for recycling. Hence, if not segregated during collection, they may pose a problem.

There is still a long way to go before developing alternate techniques to accomplish sustainability and biocompatibility in this sector. Bioplastics should be manufactured using a lower carbon footprint technology without compromising its efficiency in comparison to petro-based polymers. It can be thus concluded that advanced technology induced low priced, highly durable and completely biodegradable bioplastics would replace petro-based plastics in near future, which would unveil a new dawn of human civilization.

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Bioplastics from microorganisms

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1. Introduction

In recent years, plastics which are easily available and used are made from fossil fuel crude oil which is not biodegradable and polluting our environment day by day. To address this problem, scientists are looking for an ecofriendly biodegradable plastic material which can replace the conventional plastic. The biodegradable plastic is produced from a number of renewable plant and animal biomass. These bio-based plastics, or bioplastics, are used in making containers, food packaging, etc. It is expected that these may eventually degrade if disposed off properly.

Microorganisms have an important role to produce bioplastic from different organic sources. Bioplastics can also be generated using micro-organisms and nanometer-sized particles, particularly carbohydrate chains (polysaccharides) (Jabeen et. al., 2015). There are two main types of bioplastics, PLA (polyactic acid) and PHA (polyhydroxyalkanoate). PLA is mainly made from sugars and corn starch and PHA is mainly made from microorganisms, often genetically modified microbes (Cho, 2017). Now the use of biodegradable plastic is a necessity in many industrial applications, including food processing, agriculture, making compost bags and in sanitation. Microorganisms provide a source of bioplastics and biopolymers (polysaccharides) from renewable sources. Bioplastics are intracellularly accumulated by microorganisms as carbon and energy reserves. However bioplastics can also be produced through a biochemical process that combines fermentative secretory production of monomers and/or oligomers and chemical synthesis to generate a repertoire of biopolymers. Some microorganisms are commercially used by various industries

for production of biodegradable plastics. Examples are *Alcaligenes eutrophus* (H-16) by M/s. Zeneca Bio-Products, UK; *Alcaligenes latus* by M/s. Biotechnologische Research GmbH (Austria); Recombinant *E. coli* by M/s. Bioventures Alberta Inc. Canada (Reddy, et. al., 2003). Bioplastics are in different types based on the raw biomaterials.

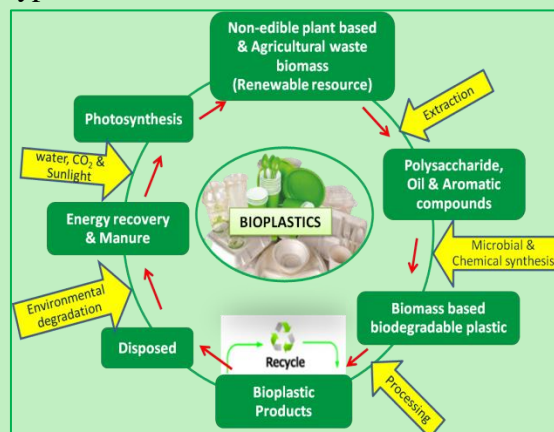


Fig.6 Flow diagram of Bioplastics (Iwata, et. al., 2021).

2. Types of Bioplastics

The most common bio-based plastics include:

(i) Starch-based Bioplastics

Typically bioplastic derived from corn or rice starch are often mixed with biodegradable polyesters. To avoid humidity absorption property of starch, flexibiliser and plasticiser such as sorbitol and glycerine are added so the starch can also be processed thermo-plastically. This types of thermoplastic starch are most widely used bioplastics, and occupies about 50% of the biolastic market.

(ii) Cellulose-based Bioplastics:

These are bioplastics derived from cellulosic materials and cellulose derivatives like, cellulose esters and celluloids.

(iii) Protein-Based Bioplastics:

These are bioplastics produced from different protein sources such as wheat gluten, casein, and milk etc.

(iv) Aliphatic polyesters

The aliphatic biopolyesters are mainly polyhydroxyalkanoates (PHA), poly-3-hydroxybutyrate (PHB), polylactic acid

(PLA) plastics etc. They are all more or less sensitive to hydrolytic degradation and can be mixed with other compounds.

✚ Polyhydroxyalkanoates (PHA)

The PHAs are linear polyesters derived through microbial fermentation of organic sugars. The micro-biotechnological process forces the specific microorganism to produce PHA as store carbon through microbial nutrient management with given high carbon source and deprived nitrogen, oxygen and phosphorous. These PHA plastics are widely used for medical applications such as sutures, slings, bone plates and skin substitutes. It is also used for single-use food packaging.

✚ Poly-3-hydroxybutyrate (PHB)

The PHB is a type of polyester produced from specific microbial process using starch, glucose and wastewater as raw material of nutrient sources.

Table 1: PHAs & PHB produced from organic sources through biotechnological process using different microbes (Marjadi and Dharaiya, 2012)

Carbon source(s)	Bacterial strain (s)	Polymer (s) produced
Glucose, sugar beet, molasses	<i>Bacillus cereus</i>	PHB, terpolymer
Glucose, technical oleic acid, waste free fatty acids, waste free frying oil	<i>Pseudomonas aeruginosa</i>	mcl-PHAs
Glucose, octanoic acid, undecenoic acid	<i>Pseudomonas putida</i>	mcl-PHAs
Glucose, soybean oil, alcohols, alkanooates	<i>Pseudomonas stutzeri</i>	mcl-PHAs
Palm olein, palm stearin, crude palm oil, palm kernel oil, oleic acid, xylose, levulinic acid, sugar beet molasses	<i>Burkholderia cepacia</i>	PHB, PHBV
Malt, soy waste, milk waste, vinegar waste, sesame oil	<i>Alcaligenes latus</i>	PHB
Malt, soy waste, milk waste, vinegar waste, sesame oil	<i>Staphylococcus epidermidis</i>	PHB
Starch hydrolysate, maltose, maltotetraose and maltohexaose	<i>Halomonas boliviensis</i>	PHB

✚ Poly(lactic acid) (PLA)

PLA is a form of transparent plastic derived from different organic sugar and starch sources through microbial enzyme activities. Through fermentation process the starch/sugar is converted into lactic acid, which is then polymerized to produce PLA plastic. This type of plastic is used in processing industry, and for production of foils, bottles, cups etc.

3. Microbial production of Bioplastic

Microorganisms are the potent producers of PHA and PHB due to their high adaptability in various extreme environmental conditions. Some bacterial species, i.e. *Bacillus* spp., *Pseudomonas* spp. and *Vibrio* spp. are efficient producers of PHB due to their higher stability and reproducibility under environmental stress conditions (Shivalkar & Prabha, 2017). Some marine salt tolerance bacteria are also capable of producing PHAs at large scale industrial level (Numata and Doi, 2012). Some haloarchaeal species belonging to genera *Haloferax*, *Haloarcula*, *Natrialba*, *Haloterrigena*, *Halorubrum*, *Halococcus*, *Haloquadratum*, *Natronobacterium*, *Natronococcus* and *Halobacterium* have found to be efficient producers of PHB (Poli et al., 2011). A number of bacterial species like *Actinobacillus*, *Azotobacter*, *Agrobacterium*, *Rhodobacter* and *Sphaerotilus* have been efficiently studied for their ability of converting organic waste to bacterial PHA. Some bacterial species, i.e. *Bacillus* spp., *Pseudomonas* spp., *Cupriavidus* spp., and *Aeromonas* spp., have been studied for efficient industrial production of PHA and PHB (Shimamura et al., 1994; Abe et al., 1994; Fuchtenbusch et al., 2000; Nagarajan, et al., 2021).

❖ Microplastic by recombinant Bacteria

Genetically modified bacteria through recombine technology synthesizes biopolymers to be used as plastics, which are completely biodegradable. Polymers such as PHBV are produced naturally by some specific bacterial strains. But the process is not viable for commercial use.

Recombinant *E. coli* strains harbouring the *Alcaligenes eutrophus* PHA biosynthesis genes in a stable high-copy-number plasmid have been developed and used for high productivity (Zhang et al., 2006).

❖ Bioplastic Production by Yeasts

About 15 strains of yeasts isolated from Kombucha tea and identified as *Saccharomyces cerevisiae*, *Candida krusei*, *Kloeckera apiculata* and *Kluyveromyces africanus* were evaluated for PHB production. PHB accumulation in these strains was found to be between 0.50% and 16.67%. (Safak et al., 2002).

❖ Bioplastic by Cyanobacteria

The cyanobacterial strain *Synechocystis* pcc6803 accumulated PHA (Sudesh et al. 2001). The PHA content was about 5% of cell dry weight. Sudesh et al. (2001) found that the biosynthesis could be improved by introducing multiple copies of heterologous PHA synthase gene.

4. Conclusion

To compensate for the environmental pollution generated by petroleum based plastic use, an alternative biodegradable plastic material is needed for a future sustainable environment. Production and extraction of bio-degradable plastics at economic and large scale industrial level is a challenge for today. Optimisation of PHB and PHA bioplastic production from suitable bio-engineered microbial strains can protect our future environment.

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FORTHCOMING EVENTS		
Event	Date	Place & Correspondence
International Conference on Environmental Biotechnology and Bioconservation	April 07-08, 2022	Athens, Greece https://waset.org/environmental-biotechnology-and-bioconservation-conference-in-april-2022-in-athens
National Conference on Advances in Science, Agriculture, Environmental & Biotechnology.	March 9th, 2022	Madurai, India. http://nationalconferences.org/Conference2022/3/Madurai/NCASAEB/
International Conference on Environmental Biotechnology ICEB	March 29-30, 2022	https://waset.org/environmental-biotechnology-conference-in-march-2022-in-paris
“BioSangam 2022: Emerging trends in Biotechnology”,	March 10-12, 2022.	Kumbh Nagari, India https://www.biosangam.in/
International Conference on Environmental Science and Biotechnology (ICESB)	May 29-30, 2022	Bhubaneswar, Odisha, India http://scienceplus.us/Conference/20126/ICESB/

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