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REVIEW ARTICLE

Eco-friendly Bioplastic for Uncontaminated Environment

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ABSTRACT
Plastics are manmade long chain polymeric molecules which are resistant against microbial attack and become part of parcel of today life. It turns out to be imperative component in agriculture as different plastics are used for various purposes namely plasticulture, polyhouses, mulches, packaging container, shrink film wrappers, etc. Plastics have replaced paper and cellulose-based products for packaging because of their strength, lightness, resistance to water and most water borne microorganism. Nowadays a wide variety of synthetic polymers are produced worldwide to the extent of ~140 million tonnes every year. Remarkable of these polymers are introduced in the ecosystem as industrial waste products every year. The dramatic increase in production and lack of biodegradability of commercial polymers, particularly commodity plastics used in packaging, industry and agriculture, focused public attention on a potentially huge environmental accumulation and pollution problem that could persist for centuries. Because of their persistence in our environment, several communities are now more sensitive to the impact of discarded plastic on the environment, including deleterious effects on wildlife and on the aesthetic qualities of cities and forests. In addition, the burning of polyvinylchloride (PVC) plastics produces persistent organic pollutants (POPs) known as furans and dioxins. In order to find alternatives, a new material has been developed known as bioplastic. Bioplastics are long chain of monomers joined with each other by ester bonds. These plastics are thus considered as polyesters. Bioplastics are classified into various types. The most common is PHA (Polyhydroxyalkonoate), which remains as a carbon and/or energy storage material in various microorganisms under the condition of deficient nutritional elements. There are a variety of bioplastic applications in the society and industries. This review paper is intended to provide information about alternatives to conventional plastics for the betterment of environment.
Keywords*: Synthetic polymers; Biodegradable; PHAs; Polyesters; Incineration*

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INTRODUCTION

In today's society it seems that the world chemistry is admired by few and frowned upon by many. Chemistry is not only thought of as extremely difficult academic disciple, but it is viewed as one of main culprits in the phenomenon known as global warming. Many global warming activists, along with the general media, stress the importance of a greener world without the use of synthetically derived chemicals. There is no denying that chemistry has had many negative impacts on our planet; however, it seems many individuals have forgotten that the science of science of chemistry has also made many beneficial contributions to our civilization. As a society we quick to criticize and point to blame, but maybe we should remember how important chemistry is as we take our daily medications, drink our coffee, and pick up our dry-cleaning [1]. Leading chemists are now taking the initiative to change modern day chemistry to help protect our environment without the lifestyles that everyone has become accustomed to. In a society where everything is going green, so is chemistry. Green Chemistry, which is also known as sustainable chemistry, "... is the design of the chemical products and processes that reduce or eliminate the use or generation of hazardous substances". Green Chemistry is set of guidelines that strive to make chemical products friendlier to the environment and to the health of all animals without having negative economic effects. Many products and processes are confirming to green standards including bioplastics.

Plastics have become a large environmental problem. In fact, "Americans go through 25 billion plastic bottles each year". Unfortunately, these plastic bottles along with other forms of plastic account for "25 per cent" of the total volume of landfills. The plastics that do residue in landfills degrade very slowly, which can cause the original products to remain in our landfills for hundreds or even thousands of years . Biodegradable plastics are becoming a new trend because they are believed to be friendlier to our environment. Biodegradable plastics are plastics that will decompose in both aerobic and anaerobic environments. Unlike conventional plastics, "a genuine biodegradable plastic will be converted to carbon dioxide, water and compost, without any persistence or toxic residue" [2]. Biodegradable plastics have the ability to significantly decrease the quantity of plastics within our landfills, and also eliminate toxins within our air from the burning of quantity of plastics within our landfills, and also eliminate toxins within our air from burning of conventional plastics [2]. Biodegradable plastics are made from renewable raw materials, and presently found in various forms with different degree of biodegradability. One of the most frequent used forms of biodegradable plastic is term as *hydrobiodegrable* plastic. Unlike conventional plastics, which are comprised primarily of starches that are found in plants or food although some contain a small percentage of synthetic polymers. When hydrobiodegradable compounds are degraded, the original product reduces to water, carbon dioxide, methane, and biomass [3].

Although methane and carbon dioxide are considered greenhouse gases, this additive effect upon the cumulative level of the planet's greenhouse gases is considered to be negligible by most researchers. This is because landfills are specifically designed to capture any releases methane, so any methane releases will be confined within the landfill. The carbon dioxide that is produced is also not looked at as a contributor of greenhouse gases because the plant that the hydrobiodegradable plastic was made from consumed carbon dioxide, so the release of carbon dioxide during the decomposition is thought of as an even exchange [3]. However, there are many other forms of biodegradble plastics that are still made exclusively from non-renewable petroleum similar to conventional plastics. This form of biodegradable plastic is termed ad *oxobiodegradable.* The primary difference between oxobiodegradable plastics and conventional plastics is that these products degrade more quickly. Oxodegradable plastics break down into water, carbon dioxide, and biomass when exposed to sunlight, heat, and other stress. Oxobiodegrables do break down much quicker than conventional plastics, but they still require the same fossil fuels during their manufacture and emit the same degree of greenhouse gases as conventional plastics [3].

The concept of biodegradable plastic products is an excellent example of green chemistry in theory, and adheres to many of many of the principles of green chemistry as set forth by the EPA. Biodegradable plastics are designed for degradation. When biodegradable products breakdown, they are supposed to completely biodegrade into safe natural compounds within a short period of time. Biodegradable breaks down much more efficiently than conventional plastics, but they are also produced much more efficiently. The production of biodegradable plastics consumes "...65 per cent less energy than producing conventional plastics. Biodegrable plastics have many environmental advantages, but they are also much safer for consumers. Biodegradable plastics are completely nontoxic, and they do not break down into toxic substances. Biodegradable plastics seem nearly perfect in theory; however, in all practically, biodegradable plastics are still their infancy, and there is a lot of room for improvement. The thought of plastics breaking down into natural compounds sounds too good to be true and it is. Biodegradable plastics do not break down in natural conditions. An individual cannot create a compost pile of biodegradable plastic in their backyard and expect to watch the plastic disappear in 90 days. Biodegradable plastics require the perfect conditions in order to decompose into natural compounds. These conditions can only be achieved in a large composting facility, which most individuals do not have access to. This implies that the majority of biodegradable plastics will find local landfills their permanent residence. Since these landfills do not meet the perfect conditions that are necessary for biodegradable plastics to decompose, the biodegradable plastics will remain in the landfill for just as long as their ancestors. There is still a lot of confusion amongst consumers and manufacturers as to what biodegradability really means. Many consumers believe that if a product is biodegradable – the product will just disappear on its own with little to no resistance. Unfortunately, biodegradable products require much resistance when it comes to biodegrading. As the truth continues to come out about biodegradable products many consumers are beginning to believe that this is just another case of false advertising.

The reluctance towards biodegradable plastics does not end at their validity. Many sceptics also believe there are moral issues that need to be evaluated. The demand for land with fertile soil will increase greatly, if the production of plastics depends on plants. If the demand for fertile soil increases than so will food prices. Currently, our economy is struggling, so an increase in food prices may not be feasible. It is apparent chemists are trying to change modern day chemistry to help protect our environment, but still there is still a lot more work and research that needs to be done until we can successfully say that there are completely "green" plastics. The guidelines set forth by the Environmental Protection Agency (EPA) are an excellent stepping stone to start changing the negative impacts that chemistry has had on our environment, but completely green chemistry is still a distant reality.

GREEN PLASTICS FOR APPROACHING DEMEANOUR

The slow biodegradation rates of plastic materials have created a need for alternative materials with physical and industrial properties similar to petrochemical derived plastics but well biodegradable.

Bioplastics are natural polymers synthesized and catabolised by various microorganisms and accumulate in microbial cells under stress conditions. Unlike petroleum- based plastics, bioplastics are eliminated from our biosphere in an environment friendly fashion. These can be conventionally managed and recycled and landfilled, or incinerated so that neither leaves plastic litter nor leads to depletion of our finite resources (fossil fuels). Moreover, these are helpful in reducing carbon footprints by as much as 40%.A number of bioplastic based on cellulose, starch and poly lactic acid (PLA) are common now a days. Starch is an inexpensive material derived from corn and other crops, and is an annually renewable source. Starch-based bioplastics can be produced by blending thermoplastic starch with biodegradable polyesters like polycarpolactone (PCL) to increase its flexibility and resistance to moisture and then can be used for foaming and injection molding. By fermentation of starch from crops, commonly cornstarch or sugarcane, lactic acid is produced which can be polymerized to produce PLA. Similarly, cellulose based plastics require wood pulps. Apart from these plastics, a number of water-soluble bioplastics are being developed like carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), pullulan, thermal polyaspartate (TPAs), etc. by modifying starch and cellulose. These are being developed to replace the water-soluble polymers prepare from synthetic monomers like acrylic acid, maleic anhydride, methacrylic acid and also by the combination of these chemically derived monomers.

Water-soluble polymers are not biodegradable, and persist in ocean, lakes, and other water depositories resulting in water pollution. On the other hand, water soluble BPs derived from modification of starch and cellulose have good moisture retention capacity and low oxygen permeability, so they easily degrade under water. Polyhydroxyalkanoate (PHA) materials are the most popular types of bioplastics. They are a complex class of polyesters synthesized by most genera of bacteria and members of the family Halobacteriaceae of the Archaea. Most of these prokaryotes synthesize poly 3-hydroxybutyric acid and other PHAs as storage compounds and deposit these polyesters as insoluble inclusion in the cytoplasm. When the cells experience a nutrient imbalance such as excess carbon with limited nitrogen, phosphorus or sulphur, PHA accumulation starts as has been shown in *Ralstonia eutropha*. The same microorganism also produces the enzyme PHA dipolymerase to break down the polymers into monomers, metabolized as a carbon source.PHB or poly hydroxyl butyrate is the most common type. However, it is a relatively stiff and brittle bioplastic and is of limited use. It can be made more flexible and tougher when copolymerized with a fraction of long chain monomers such as 3-hydroxyhexanoate (HH) or 3-hydroxyvalerate (HV), etc. and is used in wide varieties of products like containers, bottles, razors and materials for food packaging along with many medical applications such as implants, gauzes and osteosynthetic materials. In the bacterium *Ralstonia eutropha,* which is a natural PHB producer, PHB synthesis requires three enzymes and their gene products. All the three enzymes are known to locate in the cystol of the cell where PHB accumulation takes place. When the bacterium is supplemented with propionate along with glucose in the production of a copolymer [P (HB)-(HV)]. This decreases the crystallinity, stiffness and melting point of PHBs making them more suitable as commercial products.

Besides *Ralstonia eutropha,*some other strains of bacteria like *Pseudomonas putida, Comamonas acidovorans* and *Bacillus megaterium* have also been well exploited to produce these kinds of polymers. However, the major limitation associated with the production of bioplastics in bacteria is the high cost when compared to the petroleum-derived plastics. Potentially, in turn, the plant offers an alternative approach to synthesize these bulk commodity products at low cost. Whereas PHA production in bacteria and yeast requires costly fermentation process with an external energy sources such as electricity, in plant systems it is considerably less expensive as it relies on water, soil nutrients, atmospheric CO_2 and sunlight. In addition, a plant production system is much more environment friendly. While in bacteria PHB synthesis and its accumulation is limited in the cystol, in plants PHB can be produced in a number of subcellular compartments like cystol, plastids, mitochondria and peroxisomes. *Arabidopsis thaliana* was the first plant to be used for PHA production. In *Arabodopsis,* a small amount of PHB production was first demonstrated by expressing in its cytoplasm two enzymes (acetoacetyl-CoA reductase and PHB synthase) from the bacterium *Ralstonia eutropha*.The polymer produced was of high molecular weight and similar in structure and properties to PHB but the yield was low (!% of dry weight of leaves) and plants were stunned in growth. The yield was later increased from 1% to 14% dry wt. By expressing PHB biosynthetic pathways in the plastids. The achievement was ground breaking, producing one transgenic plant with 14% dry wt. of PHB in its leaves. Later on, low amount of medium chain length PHA copolymers were synthesized in peroxysomes by polymerization of 3-hydroxyacyl-CoA intermediate generated by degradation of fatty acids in peroxisomes of *Arabdiopsis* plant. After the success of synthesizing PHB in plants, PHBV copolymers were produced in both *A. thaliana* and seeds of *Brassica napus* (oilseed rape). This was one of the most remarkable feats of metabolic engineering yet performed in plants, requiring the expression of four bacterial genes (ilvA, $phaA_{rc}$, $phaB_{rc}$, $phaC_{rc}$) and modification of independent metabolic pathways (fatty acid and amino acid synthesis). But this also resulted in the lower amount of copolymer production (2.5% dry wt) compared to PHB synthesis (14% dry wt).

The reason was not clear but it had been suggested that modifying the isoleucine pathway created a metabolic burden on the plant, which decreased PHA yield. A number of other plants like Nicotiana, Brassica, Gossypium, Medicago and Elaeis have also been well exploited for synthesizing a variety of PHAs. In tobacco, by expressing in its plastids phaA and phaB genes of *R. Eutropha* and phaC gene of *Aerommas caviae,* it was also possible to produce 0.09% dry wt of PHAs. The yield was ten time more as produced in cytoplasm on Nicotiana if phaA gene alone from bacterium *R. Eutropha* and phaC gene from *R. Eutropha and* phbC gene from *A. caviae* were expressed. Plastic is often used to improve the mechanical properties of fibre-based composites. In case of cotton, *R. Eutrpha* pha genes when successfully expressed in the cystol of its fibres, the fibres from its transgenic plants contained 0.34% PHB, which was sufficient to improve the insulating properties of the fibre. Similarly, in stems of transgenic flax (*Linnum usitatissimum*), bioplastic has also been produced with an aim to improve the quality of fibre rather than providing a plant source of PHB for extraction. Interestingly, seed production as well as plant growth and morphology were found to be enhanced in these transgenic plants. At commercial level, the approach to convert plant sugar into plastic was first adopted by Cargil, an agricultural business giant, and Dow Chemicals in corn and other plants to produce a plastic called PLA (polylactide). Later on, other companies including ICI (Imperial Chemical Industry) developed ways to produce a second plastic, called PHA. Like PLA, it is made from plant sugar. Whereas PLA requires a chemical step outside the organism to synthesize it, PHA naturally accumulates within microbes as granules that constitute up to 80% of single cell mass. Following this, big industrial giants like Monsant tried to produce PHA using another approach – growing plastics in the plants. This required the modification of genetic make-up of agricultural crops and was achieved by the collaboration of researchers at Michigan State University and James Madison University in 1992 when they genetically engineered *A. thalina* plant to produce a brittle type of PHA. But this plastic turned out to be very costly than fossil fuel based counterparts. However, the challenges of separating the plastics from the plants, too, are formidable. All the processes required to isolate plastic from corn stover consume even more fossil fuel than most petrochemical manufacturing routes. The only plant based plastic that is being commercialized is Cargill Dow's PLA. The hope behind green plastics research is to find methods of producing commercially viable replacement for petrochemical polymers through the metabolically engineered action of plants. Thus, researchers have turned toward plants as being a potentially cheaper and more convenient method of producing renewable, biodegradable plastics. A broad range of PHAs covering a spectrum of physical properties have now been synthesized in plants. The challenge for the future is to succeed in high-level production (15% dry wt) of a limited number of useful PHAs and in developing efficient extraction processes.

Plastics are consumed in almost every place such as, in routine household packaging material, in bottles, cell phones, printers, etc. it is also utilized by manufacturing industries ranging from pharmaceutical to automobiles. They are useful as synthetic polymers because, their structures can be chemically manipulated to a variety of strengths and shapes to obtain higher molecular weight (MW), low reactivity and long durability substances. Plastics are important materials for the society not only because of their higher MW and low reactivity but also for their durability and cost efficiency. Unfortunately these petroleum based plastics are not biodegradable. This result in one of the major causes of solid waste pollution through buried in landfills. They are indigestible and in many cases the animals die due to plastics blockage in the gut. Furthermore; Plastics are often soiled by food and other biological substances making physical recycling of this material undesirable. Incinerating plastics has been one option but other than being expensive it is also dangerous; various harmful chemicals like hydrogen chloride (HCl) and hydrogen cyanide (HCN) are released during its incineration, Johnstone [12]. In recent years, there has been increasing public concern over the harmful effects of petrochemical derived plastic materials in the environment. Problem of managing plastic waste on the earth is increasing very rapidly now a days, and studies have been initiated to find out suitable eco-friendly materials to minimize environmental problem, Madison and Huisman [4].

INEVITABILITY OF DEGRADATION

Some synthetic plastics like polyester polyurethane, poly ethylene wit starch blend, are biodegradable, although most commodity plastics used now are either non-degradable or even takes decades to degrade. This has raised growing concern about degradable polymers and promoted research activity worldwide to either modify current products to endorse degradability or to develop new alternatives that are degradable.

Degradation of plastics occurs due to any physical or chemical change in a polymer as a result of environmental factors, such as light, heat, moisture, chemical conditions or biological activities.

Degradation has been reflected in changes of material properties such as mechanical, optical or electrical characteristics viz. crazing, cracking, erosion, discoloration, phase separation or delamination. The changes include bond scission, chemical transformation and formation of new functional groups. The degradation will either be photo, thermal or biological.

- **Photodegradation:** Sensitivity of polymers to photodegradation is related to the ability to absorb the harmful part of the tropospheric solar radiation. This includes the UV-B terrestrial radiation (~295 – 315nm) and UV-A radiation (~315 – 400nm) which are responsible for the direct photodegradation (photolysis, initiated photooxidation). Visible part of sunlight (400 – 760nm) accelerates polymeric degradation by heating. Infrared radiation (760 – 2500nm) accelerates thermal oxidation. Most plastics tend to absorb high energy radiation in the ultraviolet portion of the spectrum, which activates their electrons to higher reactivity and causes oxidation, cleavage, and other degradation.
- **Thermal degradation:** As a result of overheating, molecular deterioration of polymers takes place. At high temperatures the components of the long chain backbone of the polymer can begin to separate (molecular scission) and react with one another to change the properties of the polymer. The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. Thermal degradation generally involves changes to the MW (and MW distribution) of the polymer and typical property changes include: reduced ductility and embrittlement, chalking, color changes, cracking and general reduction in most other desirable physical properties.
- **Biodegradation:** In this process organic substances are broken down by living organisms. The term is often used in relation to ecology, waste management, bioremediation and to plastic materials, due to their long life span. Organic material can be degraded aerobically, with oxygen, or anaerobically, withot oxygen. A term related to biodegradation is biomineralisation, in which organic matter is converted into minerals. In contrast to photodegradation which leads to breakdown of the polymers into non-degradable smaller fragment leading to loss of structural integrity of material, biodegradation leads to complete decomposition of polymers.plastics are biodegraded aerobically in wild nature, anaerobically in sediments and landfills and partly aerobically and partly anaerobically in composts and soil. The main advantage is that, the biodegradable polymers are completely degraded to water, carbon dioxide and methane by anaerobic microorganisms in various environments such as soil, sea, lake water and sewage and hence, is easily disposable without harming environment while carbon dioxide and water are produc**e**d during aerobic biodegradation. Generally, the breakdown of large polymers to carbon dioxide (mineralisation) requires several different organisms, with one breaking down the polymer into its constituent monomers, one able to use monomers and excreting single waste compounds as byproducts.

To find alternatives researchers have developed fully biodegradable plastics, which are disposed in environment and can easily degrade through the enzymatic actions of microorganisms. The degradation of biodegradable plastic produces carbon dioxide (CO_2), methane (CH_4)), water (H_2O), biomass, humic matter and various other natural substances which can be readily eliminated. Due to its ability to degrade in the biotic environment these types of materials are renamed as "Bioplastics."

PLASTIC THAT DO THE VANISH ACT

Wouldn't it be wonderful if plastic could disappear into thin air after use? An Australian company has done just that it has come up with a novel plastic packaging product that on coming in contact with water, literally vanished into thin air. Manufactured by Plantic technologies, this biodegradable has the same look-and-feel and properties of strength, stability, and shape like that of conventional plastic. What sets it apart formats petrochemical counterparts is that Plantic is made of maize-commonly used to make bread and pasta. It is this composition that makes Plastic renewable, sustainable, and nontoxic. Plantic is the world's first, truly environment-friendly plastic that is competitive in terms of cost and functionality with petrochemical-based plastics. What's interesting is that this plastic does not solely depend on professional composting facilities for degradation. *Source: Terragreen*

MAKING BIOPLASTIC FROM POTATOES: The bioresearchers at Maine University (MU) of UK have developed a novel method for making bioplastic from starch obtained from potatoes. During the process of making the processed foods from potatoes, large quantities of leftover are obtained as waste which can be used for making bioplastic. The whole process is very complicated, however the leftover potatoes waste is crushed into a pulp in a big grinding machine. The starch obtained from this pulp is converted into glucose. Lactic acid in large quantity is added to this. Then by subjecting this mixture to an electrically charged refinement process and there after passing it through carbon filters, a powder-like substance is obtained from which bioplastic is made. According to the report of Chase Smith Policy Centre (CSPC) of UM due to the natural property of being biodegradable, the bioplastic obtained by this method is environment-friendly, i. e. unlike the conventional plastic it will not pollute the environment by remaining there for a long period. The report also states that the bioplastic obtained from potatoes can be used for making bottles, packets and all sorts of decoration objects, Mukherjee [5].

BIOPLASTIC AND SOCIAL BENEFITS

What makes bioplastic especially important is that petroleum oil price is increasing tremendously and its stock will end in the near future. It is important for the global community to have an alternative for the product derived from petroleum oil such as plastics. PHAs at least will be a solution for the most of the industries and society, which largely depend on materials made from plastic. No new inventions can escape fro the limitations and drawbacks and bioplastics too have some drawbacks. The most important drawback for PHA production is its production cost, but the good news is that the price of PHA production is decreasing, whereas, petroleum oil price is increasing constantly, Kumar et al. [6]. As a result, the gap between the petroleum oil and PHA are becoming very narrow. The first potential application of PHA polymers was recognized in the 1960s. PHA patents cover a wide range of PHAs products such as coating and packaging, bottles, cosmetic containers, golf tees, and pens, Webb [7]. PHAs have also been processed into fibers, for a non woven fabrics material, Son et. al. [8]. PHAs can be used for all sorts of biodegradable packaging materials, including composting bags, food packaging, sanitary articles like diapers and fishing nets, Javed and Gruys [9], biodegradable rubbers, Walle et. al. [10]. PHAs are also used to develop scaffold for tissue engineering, Simmon et. al. [11], and also posses numerous applications in pharmacy and medical science.

CONCLUSION

Researchers started to look if plastics could be designed to become susceptible to microbial attack, making them degradable in a microbial active environment. Biodegradable plastics opened the way for new considerations of waste management strategies since these materials are designed to degrade under environmental conditions or in municipal and industrial waste treatment facilities. However, the production cost of PHA is quite high compared with that of synthetic non-biodegradable, and so great effort has been recently devoted to making this process economically more feasible, for instance, by changing the substrate from glucose to renewable resources. The synthesis of PHA in crop plants can be regarded as a promising alternative for the large scale and low cost production of this polymer. Changing the carbon source and bacterial strains for biopolymer production with properties ranging from stiff and brittle plastics to rubbery polymers is one way of cost reduction. However, bioplastics can have its own environmental impacts, depending on the way it is produced. Hence there is an urgent need to develop efficient microorganisms and their products to solve this global problem with plastics.

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