Global Scientific JOURNALS

GSJ: Volume 9, Issue 5, May 2021, Online: ISSN 2320-9186
www.globalscientificjournal.com

REVIEW OF BIOPLASTICS FOR A SUSTAINABLE FUTURE

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Key Words

Bio-based, Biodegradability, Bioplastic, Biopolymer, Sustainable.

ABSTRACT

The diminishing sources of fossil fuel and the environmental pollution that the petroleum based plastics that are made from the finite resource has prompted the need for an eco-friendly alternative that has come in the form of bio-based plastics and biodegradable plastics. The biodegradable plastics will aid in alleviating some of the burden that comes from synthetic plastic pollution while bio-based plastics will aid by alleviating some pressure from the non-renewable feed stock that is fossil fuel with a renewable feed stock. Till date bioplastics have been in development and slowly aging momentum in the global commercial market. With the development has come a diversification and discovery of properties which renewable sources have to offer in the production of bioplastics. Bioplastics now have a large range of applications in industries such as automotive, agriculture, packaging, consumer electronics, medical, cosmetic and housewares. All this has been made possible through a diverse range of modification of the source materials for the bioplastics. In this review, degradation of plastics, classification, modifications and applications of bioplastics are discussed.

1. Introduction

Synthetic polymer plastics or petrochemical-based plastics can be defined as man-made polymers composed of a petroleum based matrix (20). Synthetic plastics have a widespread use on a global scale due to their advantages which include: durability, versatility, inertness, ability to be colored, light in weight, low cost, and good mechanical and thermal properties. (33,38).Despite their numerous advantages, synthetic plastics still have disadvantages to their use, namely:

i. Manufacture of synthetic plastic is dependant on crude oil which is finite and rapidly diminishing (1,11).

ii. Recycling of conventional plastics is difficult due to the numerous and complex modifications they undergo during manufacturing leading to plastic not recycled being discarded in dumps and landfills (20,37).

iii. Slow rate of degradation due to the chemical structure of conventional plastics lads to great accumulation in the environment (20,33).

iv. Incineration of plastics leads to release of toxic chemicals into the air (1).

v. Destruction of biodiversity due to accumulation of plastic waste in the environment (33).

These disadvantages led to the need for development of biodegradable plastics and bio-based polymer products. The European Standard EN16575 defines Bio-based products as "Products wholly or partly derived from biomass such as plants, trees or animals (the biomass can have undergone physical, chemical or biological treatment)". Biomass can be defined as any biodegradable organic material which has been derived from a living organism such as plants or animals (pp.1). Misra et al.,(2011), defined a bioplastic as "a material that are either biodegradable, derived from both renewable and non-renewable resources or materials that are non-biodegradable and derived from renewable resources"(pp.2). A biodegradable plastic is one which undergoes the process of biodegradation which involves the action of microorganism naturally available on it and converting the material into substances such as water, carbon dioxide, compost and other natural substances(3, 9, 44).

The development of biodegradable plastics has sparked the creation of anew branch of chemistry known as "green chemistry "or "sustainable chemistry". This branch involves the designing and creation of chemical products and processes which reduce and/or eliminate the creation of substances that would cause the destruction of biodiversity, inefficient use of energy and high waste generation (17, 36). Bioplastics have an number of advantages to their use, such as: biodegradability (3), compostability (31), compatibility , non-toxicity, ionic selectivity, adsorption a, bio-adhesion (38), and low cost feed stock for raw materials (8).

Along with the above advantages, the development of bioplastics and their use has increased also due to a number of factors. These are:preference of consumer to use biodegradable and bio-based plastics (3,31), legislative drivers towards green procurement, such as, governments banning use of conventional plastic bags (3,31), and they offer particular features that are specific to an application , such as, bio-adhesion in bio-medicine (31, 38).However bioplastic development also faces a number of barriers preventing the progression. These are:

a. Pressure placed on agriculture sector as with rise in demand of bioplastics there is added competition between the use of agricultural land for food or for raw materials (1,3).

b. Poor and low performance characteristic of the bioplastics in comparison with conventional plastics such as thermal instability, chemical instability, hydrophilicity (13,38).

c. High cost of processing leading to an expensive product. (3,31)

Plastic abbreviation	*Plastic name*
PE	Polyethylene
PET	Polyethylene terephthalate
PS	Polystyrene
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PLA	Polylactic acid
PCL	Polycaprolactone
PBSA	Polybutylene succinate-co-adipate
PBAT	Polybutylene adipate terephthalate
PP	Polypropylene

PEA	Polyesteramides

Table 1: Plastic names and their abbreviations

2. Classification of Bioplastics

Bioplastics can be classified based on their origin and synthesis process (44).*Figure 1* is a summary of the biodegradable and non-biodegradable polymers used in the manufacturing of plastics.

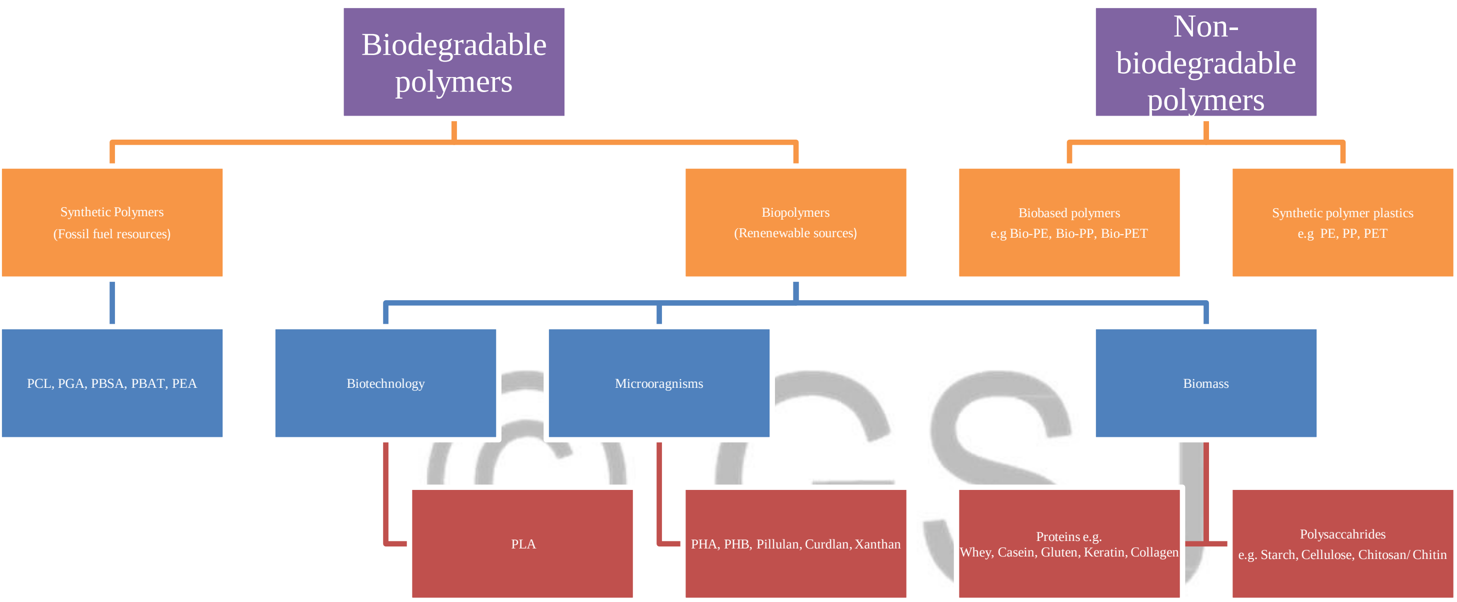

Figure 1: Classification of biodegradable and non-biodegradable plastics polymers

2.1 Biodegradable polymers

These are bio-based and petrolatum-based polymers which undergo biodegradation.

2.1.1 Biodegradable Synthetic polymers

Synthetic polymers are composed of monomers which have been derived from the chemical synthesis of fossil fuels but are biodegradable. Some examples of these biodegradable synthetic polymers include: Polybutylene adipate terephthalate (PBAT) polycaprolactone(PCL), polyglycolic acid(PGA), polybutylene succinate-co-adipate (PBSA), polyesteramides (PEA).(41,44)

2.1.2 Biopolymers

A biopolymer is a polymer comprised of long length of repeating chemical blocks produced by living organisms (3).

a. *Biomass derived biopolymers*

These biopolymers are derived from the natural polymers found in animals, marine and agricultural sources(32). They are then further categorized into the type of polymers they comprise of such as polysaccharides (32), proteins (44), lipids (24) and nucleic acids (3).

Starch

Starch is one of the most abundant natural polymer and renewable resource. Mostly derived from plants biomass where it is produced during photosynthesis in the chloroplasts (35). Starch is derived as stored polysaccharides of legumes, cereals and tubers(13).Starch undergoes some modifications in order to improve its natural properties and ease its processability. These modifications may include: use of flexibilizers and plasticizers such as glycerol and sorbitol, blending with other materials such as polymers, and genetic or chemical modification.(13, 32)

Cellulose

Cellulose is a naturally abundant and renewable polysaccharides found in plants and is derived through delignification of wood pulp or cotton linters. Cellulose is difficult to process and as such undergoes modifications like chemical treatments with NaOH, CS_2, H_2SO_4 to form cellophane. Derivitization is another method of modifying cellulose which involves the deriving of cellulose from a solvated state via etherification of hydroxyl groups or esterification. Examples of cellulose derivatives are: hydroxypropyl cellulose, hydroxypropyl methyl cellulose and carboxymethyl cellulose.(13,32)

Proteins

Proteins are composed of amino acids and can be obtained from both plant and animal sources. Some examples of plant proteins include soy, and wheat gluten while animal proteins include whey, keratin, casein and gelatin(32,44). Protein-based bioplastics show advantages such as excellent gas barrier properties, low processing temperature and high tensile strength. They do however face the major shortcoming of being highly hydrophilic and as such require alterations in structure which can be done by chemical or microbiological modifications and blending with other polymers(15,22,32).

Chitosan/Chitin

Found naturally in crustacean shells, on the exoskeleton of arthropods, and in the cell walls of fungi and yeast, chitin or poly (β(1-4)-N-acetyl-D-glucosamine) is the second most abundant polysaccharide resource after cellulose. Chitosan can be derived from chitin via N-deacetylation of chitin.(19,21,32

b. Microorganism derived biopolymers

These are naturally occurring organism-based biopolymers formed from the fermentation of carbohydrates or lipids from plant-derived feedstocks by microorganisms with the product formed being extracted and used to form biodegradable polyesters such as Polyhydroxyalkanoates (PHA) and Polyhydroxybutyrate (PHB). PHA/PHB are extracted by use of solvents such as: methylene chloride, chloroform, or propylene chloride (19, 41). PHB is the most prevalent type of PHA and is formed from the polymerization of the monomer 3-hydroxybutyrate and degrades in both anaerobic and aerobic conditions (32). PHA's are biodegradable by action of PHA hydrolases and PHA depolymerases. Aside from their ability to biodegrade PHA has numerous qualities that make it of great use in multiple industries including packaging,these include:biocompatiblility, thermostability,printability,dyeability, flavor and odor barriers, non-toxic,heat seal-ability, and resistance to grease and oil.PHB has great characteristics such as optical active,gas barrier properties, and water permeability(32,44).

c. Biotechnology derived biopolymers

These are polymers which have been synthesized chemically from bio-based monomers.

Polylactic acid (PLA)

PLA is a thermoplastic alliphatic polyester (13).Obtained from the fermentation of carbohydrates such as corn and sugar beets into lactic acid or from synthesis of petrochemicals(32,44). PLA is synthesized in two ways, namely: condensation polymerization of lactic acid to form low molecular weight PLA, or by ring-opening polymerization of a lactide which forms high molecular weight PLA (13,44). It is widely used as an alternative to conventional plastic such as high density polyethylene (HDPE) and low density polyethylene (LDPE), polystyrene (PS) and polyethylene terephthalate (PET) (41). It is widely used due to its qualities,namely: stiffness, transparency, processability and bio-compatibility (44).

2.2 Non-biodegradable polymers

These comprise of bio-based as well as petroleum-based polymers which are non-biodegradable.

2.2.1 Bio-based polymers

Despite of a plastic being bio-based, its ability to degrade will solely depend on its structure and physical properties (3). Examples of non-biodegradable plastics that are bio-based include: bio-based-polyethylene (Bio-PE), bio-based-polypropylene (Bio-PP), and bio-based-poly(ethylene terephthalate) (Bio-PET). These are made by the conversion of renewable resources such as starch into building blocks for synthetic polymers (3). The main reasoning for creation of these is to ease the pressure put on the feed stock required for the creation of synthetic polymer plastics as fossil fuels are finite.

2.2.2 Synthetic polymers

These are what are commonly known as “traditional plastics” or “conventional plastics”. Comprised of monomers derived from the petrochemical industry to form a polymer that is non-biodegradable due to their chemical structure (37). Example of synthetic polymer plastics include: polyethylene (PE), polypropylene (PP) and polystyrene (PS) (14).

3. Modifications of Bioplastics

In order for bioplastics to be able to compete fairly with conventional plastics, they must be able to offer the same performance that conventional plastics offer while still overcoming the shortcomings of synthetic plastic use of dependence on a non-renewable source and/or pollution. To do this the biopolymers and biodegradable synthetic polymers have to undergo modifications.

i. Creation of chemical linkages with organic compounds

This involves the introduction of small functional groups to the chemical structure of the bioplastic in order to alter a particular feature in the bioplastic (38).

ii. Blending of the bioplastic with other polymers

This involves the creation of a new material by combining polymers in order to make a product with superior physio-chemical and mechanical properties (38).Blending of starch with polymers such as polyolefins, polyhydroxyalkanoates (PHA), polylactide (PLA) and polycaprolactone (PCL) has seen the enhancement of mechanical properties as well as the water resistance of starch(44).

iii. Cross-linking

This involves addition of a cross-linking agent to the functional group of a bioplastic using cross-linking strategies such as photopolymerization, heat gelatinization, and the addition of a cross-linking agent (38).

iv. Grafting reactions

This involves the grafting of a copolymer of a monomer onto the main polymer chain of a bioplastic (38).

v. Biocomposite or nanocomposites

IUPAC defines a composite as "multicomponent material comprising multiple, different (non-gaseous) phase domains in which at least one type of phase domain is a continuous phase." Thakur and Singa (2010) defined a biocomposite as a material of whose phase composition is one of biological origin. Nanocomposites are composite materials which have at least one phase dimension of the order of nanometers(12). A hybrid composite material is a material formed from the combination of multiple phases with at least two reinforcement elements being integrated into a matrix (6). The use of natural lignocellulosic composite to achieve improvement in properties has gained a large interest in replacing synthetic plastics in various applications as they act as reinforcement agents(4). The use of nanocomposte precursors has also become an option in terms of modification with silicates being the most widely research (38)

4. Degradability

Degradation is the process by which a polymer undergoes a cleavage of its bonds (34)

There are two main types of mechanisms by which materials undergo degradation namely biotic e.g.,biodegradation and abiotic e.g., Oxo-degradation, Hydro-degradation, Chemical /Chemo-degradation and Photo-degradation.

4.1 Biodegradation

Involves the biological process in which microorganisms dispose of the carbon substrates in materials by using them as food for their life processes (26). The mechanism of biodegradation involves microorganisms in a disposal environment breaking down the material into smaller molecules and oxidizing them to CO_2 and water, and releasing energy (3).

Experimental data is currently available on numerous ways in which biodegradation takes place by different forms of living organisms. Lee et al., (2005), observed the degradation of Bioplastic Poly-3-hydroxy-butyric acid (PHB) in the presence of Fungi.The biodegradation of the bioplastic Poly(DL-lactic acid) was observed by Panyachanakul et al., (2019) in which the bioplastic underwent microbial degradation by enzymatic action from the bacterial strain T16-1 of *Actinomadura keratinilytica* resulting in a weight loss of up to 99.93% of the bioplastic.Biodegradation by Phyllosphere yeasts of bioplastics poly-butylene succinate and poly-butylene succinate-co-adipate has also been observed (16).

The main reason as to why biodegradation is being considered more than other types of degradation is mainly driven by the manner in which plastics are disposed off in the environment. A "disposal environment" is thus a main factor in the designing and reporting of a biodegradable product. Example of disposal environments include composting environment, soil environment, anaerobic environment such as an anaerobic digester or landfill and marine environment (26, 44).

4.2 Abiotic types of degradation

These are degradation processes which are non-biological in their mechanism (26).

4.2.1 *Oxo-degradation*

Oxo-degradable plastics have additives which are oxo-degradable included in their structure causing the degradation process to be initiated by exposure to oxygen and acceleration to the degradation in presence of light and/or heat (3).

The general oxo-degradation mechanism takes place in three stages:

Stage 1: Initiation

RH(heat, oxygen, stress)→ROOH

ROOH(heat and/or UV light)→RO$^\bullet$ + $^\bullet$OH

PH→RPOH(H2O)

Stage 2: Propagation

$R^{\bullet}+O2 \rightarrow RO_2^{\bullet}$

$RO_2+RH \rightarrow ROOHR^{\bullet}$

Stage 3: Termination

$2R^{\bullet} \rightarrow R-R$

$R^{\bullet} + ROO^{\bullet} \rightarrow ROOR$

$2ROO^{\bullet} \rightarrow O_2 + ROH + R{=}O$

This particular degradation process involves a total change of molecular structure of the material to a point where no fragments or toxic residues are left upon completion. The only products will be CO_2, water and biomass(3).

4.2.2 Hydro-degradation

Hydro-degradation involves the decomposition of bonds by hydrolysis due to exposure to water and moisture resulting in a reduction in the material's molecular weight(30,42,43.

4.2.3 Photo-degradation

Photodegradation involves the action of light on a material where a photochemical reaction takes place after the absorption of UV radiation by carbonyl groups in a material. The process of photodegradation can be accelerated or the material more susceptible to it if in contact with oxygen and/or water. It causes deterioration of mechanical properties, loss of flexibility and discoloration(5,23,27,40).

4.2.4 Chemical degradation

Chemical degradation involves the full or partial depolymerization of a polymer to monomer or oligomers and other chemical substances respectfully. (39)

5. Applications of Bioplastics

Bioplastics plastics feature in a variety of commercial applications in a large array of industries ranging from medical to agricultural, automotive, pharmaceutical,consumer electronics and packaging industries.

5.1 Packaging

Packaging encompasses the storage, handling, transport and preservation of product quality in order to sustain the supply chain (11). Synthetic plastics have been in use for the purpose of packaging due to their ability to overcome the limitations faced by bioplastics such as low cost (13), oxygen/water vapor barriers (44), superior mechanical performance (32), carbon dioxide, anhydride, and aroma compound barrier (32) and thermal resistance (28). Some of the most popular synthetic plastics in packaging are PE, PET, PP, polyamide (PA), polyvinylchloride (PVC), and polystyrene (PS) (32,44) Despite its numerous advantages over bioplastics, synthetic plastics still face the major burden of non-biodegradability which leads to pollution. Thus the need for biodegradable plastic has risen as they can be able to undergo degradation naturally (32).

Multiple bioplastic materials have been generated into packaging by use of conventional plastic processing techniques such as extrusion (44), compression molding, injection molding (41), thermofoaming (13), and blow molding (32,44). On top of gaining versatile processing techniques bioplastics have also undergone modifications in order to make them better at performance delivery. Packaging comes in many forms be it food packaging, medical packaging or even toy packaging, and as such the bioplastic needs to satisfy the need presented by the product being packaged (3).

5.1.1 Food Packaging

Food packaging has seen the greatest demand in the use of bioplastics due to its ability to biodegrade seeing as currently most food packaging is for sing-use only (69). Some of the most important purposes for food packaging are: protection of food from contaminants, preservation of food quality throughout shelf life, ensuring safety from mechanical damage and sharing of information related to the food product such as nutritional value (32).Some examples of bioplastic materials currently in use in the food packaging industry include polylactides, starch e.g. Ecoware (35,44), cellulose derivatives (10), and biodegradable polyesters (10).

5.1.2 Antimicrobial packaging

Antimicrobial packaging involves the incorporation of an antimicrobial agent within the system of the packaging material in order to deactivate or reduce the growth of harmful microbes.Antimicrobial packaging is mostly use wit food and hygiene products (10,44). Ways in which antimicrobial packaging can be prepare include integration of bioactive agents directly into the packaging compounds, production of reactive oxidizing species through surface irradiation of the polymer matrix, coating the packaging material with a bioactive agent, through gas emission/flush via modified atmosphere packaging, through use of bioactive resin and via film forming using antimicrobial polymers(10,44).

5.2 Automotive and aerospace applications

In line with the change of fuel type as well as consumption and emission, automotive and aerospace industries are developing ways to replace synthetic plastics components with bioplastics . Bio-based polyesters a, bio-based poly propylene and bio-based polyamides are some examples of bioplastics currently used in these industries serving as high quality alternatives that meet the criteria of performance used with conventional plastics.Toyota is a good example of a leading automotive brand that has integrated the use of bioplastics such as bio-based PET and PLA blends in its production process (3).

5.2 Medical

In the biomedical industry bioplastics are used in multiple medical devices and materials, such as

i. Non toxic biodegradable polymer sutures which dissolve and metabolize in the body.Example of bioplastic material used in the making sutures include : polylactic-co-glycolic acid (PLGA), PLA-based and poly-L-lactic Acid (PLLA)-based composites (2.3)

ii. Drug delivery systems are novel materials or carrier systems which enable a therapeutic substance to be introduced into the body and improves its efficacy and safety by controlling the rate, time and place of release of drugs in the body.(7,25).Example of bioplastic material used in the making of drug delivery include: PLGA for cancer drug delivery systems (2).

iii. Biodegradable pins, tacks and screws (3)

iv. Biodegradable bone plates (3)

v. Plain membranes for guided tissue regeneration(3)

5.3 Consumer electronics

Bioplastics are being used in a variety of consumer electronics, namely: circuit boards, data storage devices, casings, touch screens, loud speakers, keyboard elements, vacuum cleaners and the mouse on a laptop.An example is the use of PLA blends in the making of monitor screens. (3)

5.4 Agriculture and horticulture

Bioplastics have been used in multiple agricultural applications including : Mulches which are used in creating a microclimate around a plant which in turn aids by increasing soil temperature, controlling weeds as well as the conservation of moisture.e.g. Solaplast ; Seeding strips; Agricultural tape e.g. BUDDY TAPE®; Foils and hail nets; Green house cover an solarisation films (3,26).

6. Conclusion

This study has synthesized the current scientific literature regarding bioplastics classification,degradation, modifications and applications. The use of Bioplastics whether bio-based and biodegradable or bio-based and biodegradable has advantages attached to each and as such would be a great alternative to the conventional plastics. Great progress has been made in terms of development and modifications as well as the sourcing of new feedstocks for bioplastics. Though with the use of modification comes the disadvantage of most products labeled as biodegradable either being degraded into nano-particles and not actually being incorporated back into the disposal environment or once degraded harmful products are released as a result of the additives used to modify the bioplastic.Therefore, the field of bioplastics still need a lot more research to be done especially regarding the biodegradability parameters as well as the choice of additives made regarding modifications.

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