



Review Article



Polyhydroxybutyrates (PHBs): an eco-friendly alternative to petroleum-based plastics for diminution of their detrimental effects on the environment

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ABSTRACT

Human has been known to use different types of polymers in their daily routine for ages, among which plastics that are derived from fossil fuels or petroleum occupies a greater part. The domestic, as well as commercial use of plastics, has been known so far globally. Plastics are used for packaging, making utensils, household items, portable machines, spare parts, medical stents, spectacles, sportswear, cellphones, golf balls and many other items. Despite knowing the negative and fatalistic effects of plastics, we humans have become dependent on plastics for our daily routine welfare. The major reasons for this are durability, inertness, lightweight, thermal and electrical insulation, resilience to corrosion and readily moulding into multifarious shapes. But the non-biodegradability of this polymer has led to many environmental issues that have detrimental effects. So there is a need to switch from non-biodegradable plastics to biodegradable ones to reduce these harmful effects without the replacement of other properties of petroleum-based plastics that makes it one of the most commercially used polymer. Biodegradable plastics have gained a lot of attention over a shorter period. These include Polyhydroxybutyrates (PHBs) and Polyhydroxyalkanoates (PHAs) majorly. These are biodegradable along with all the properties that petroleum-derived plastics have which makes them a finer and eco-friendly option. The present review focuses majorly on PHBs and summarises their physical properties, biosynthesis and different methods of industrial production, extraction, PHB-based biocomposites and/or nanocomposites along with their applications and prospects.

Keywords: Plastics, Biodegradable plastics, PHBs, PHAs, biocomposites, nanocomposites.

INTRODUCTION

Humans consume enormous amounts of polymers in the form of plastics daily. (Lee *et al.*, 2021). Plastics are used widely throughout many industries and have practically become necessary, yet their ever-increasing use has negative environmental effects (Vlaeminck *et al.*, 2022). Globally, people are becoming more and more conscious of the negative effects that excessive use of plastic materials in daily life has on the environment and human health. (Sirohi *et al.*, 2021) Traditionally, ethylene and propylene products derived as functional derivatives from fossil hydrocarbons have served as the foundation for the monomers utilised in the wide synthesis of polymers. (Anjana *et al.*, 2021). Single-use plastics (SUPs) are materials made from fossil fuels that are often used in the food, beverage, and agriculture industries and are intended to be thrown away right away after usage. It has historically been difficult to recycle plastics, which are frequently made of polypropylene, polystyrene, or polyethylene, and present garbage collection systems are unable to securely and properly dispose of our recycled waste material on a worldwide scale. Therefore, these

SUPs that sweep up in landfills gradually enter our ecosystems, seas, and food chain, adding to society's escalating issues with plastic pollution (Eriksen *et al.*, 2014, Chen *et al.*, 2021). By 2023, it is anticipated that demand for these biomaterials would increase to 9.45 million tonnes, which will encourage people to use less synthetic polymers and create biopolymers in a sustainable and circular fashion instead. (Herrera *et al.*, 2021).

Recycling is done in certain circumstances to reduce these disposal issues because plastics cannot degrade; nevertheless, this is not a good solution. (Das *et al.*, 2021) Only 26% of the 33 billion tonnes of plastics manufactured globally are expected to have been recycled by 2050, according to the latest estimates. (Hernandez *et al.*, 2021) The total amount of production in 2019 was around 360 million tones. (Ryan 2015) Since many polymers are derived from crude oil, the rising demand for plastics not only increases oil consumption, placing additional stress on depleting reserves but also pollutes the environment during disposal (more than 302 million tonnes of plastic were

wasted in 2017) due to the typically challenging and drawn-out process of degradation of these materials and their composites. (Schlebrowski *et al.*, 2021) The creation of fully biodegradable plastics and the switch to them is critical to minimize the increasing pollution brought on by our usage of plastics. (Hernandez *et al.*, 2021) Due to society's and governments' concern for the environment, the use of biopolymers as environmentally benign materials to replace conventional polymers has garnered attention. Polyhydroxybutyrate's (PHB) ability to biodegrade makes it a superior option for substituting petroleum-based polymers. One of the primary challenges to PHB's success in the polymers industry is that they are significantly more expensive than traditional polymers. (Ortriz *et al.*, 2020). The alternate strategy is to select carbon substrates that are sustainable, economically advantageous, and easily accessible for maximal PHB production. Agricultural waste products provide both reasonable carbon and nitrogen sources, which significantly lowers the cost of producing PHB (Brodjnak *et al.*, 2016). PHAs can be utilised in biocomposite materials, which combine bio-based agro-residues, to cut costs while retaining performance in certain industries, such as agriculture, food, and medicine. According to Menossi *et al.* (2021), bio-based composites are described as composite materials made of two or more separate biodegradable phases. These phases typically include a continuous weak matrix and embedded reinforcements that provide strength and stiffness. The advantages of PHA-based biocomposites strongly support future studies in this field. There is an urgent need to produce biodegradable biopolymer-based bio-composites that may be utilised as a coating material for food packaging. This paper provides an in-depth analysis of PHA blending, which is more effective in enhancing its properties and resulting in better production and higher quality-based usage (Kumar *et al.*, 2021).

Polyhydroxybutyrate

Biopolymers are made from biological materials, are biodegradable, or have both of these properties. The most promising polymers for providing a comprehensive sustainable replacement for plastic packaging are biopolymers. The most sustainable group includes polyhydroxyalkanoates (PHAs), which are both biobased and biodegradable. (Gracia *et al.*, 2022) To address the environmental problems caused by nondegradable plastics, PHAs have been suggested as a partial replacement for conventional petrochemical plastics like polyethylene (PE), polypropylene (PP), and polyethylene terephthalate (PET) (Tan *et al.*, 2021). The bacterial strain, carbon feedstock, and growth conditions utilised all affect the monomer structure and physicochemical characteristics of the various PHAs. Currently, it is known that there are more than 150 distinct PHA monomers, with 3-hydroxybutyrate (3HB) and 3-hydroxy valerate (3HV) being the two most prevalent (Gracia *et al.*, 2022). French scientist Maurice

Lemoigne characterises poly-hydroxybutyrate (PHB) for the first time in 1923 (Yeo *et al.*, 2018).

Many prokaryotes produce this highly crystalline, biodegradable, linear polyester as lipid stores at times of impending stress, such as when there is an abundance of carbon sources available and no other nutrients, such as nitrogen, oxygen, sulphur, phosphorus, etc (Thapa *et al.*, 2019).

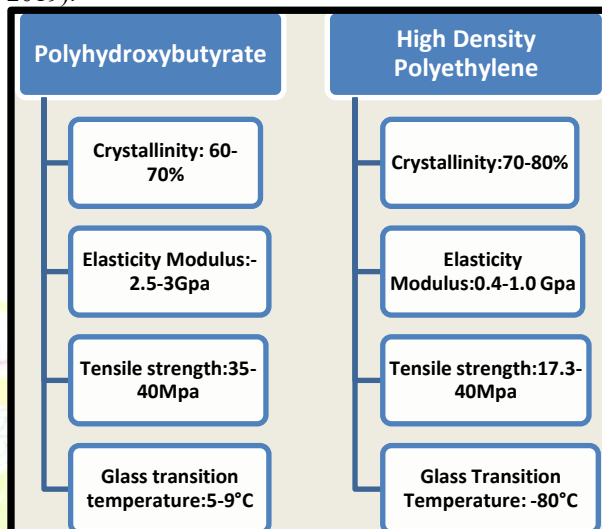


Fig.1. Comparison of physical characteristics of Polyhydroxybutyrate and High-density Polyethylene

Unlike traditional polymers, biodegradable polyhydroxybutyrate (PHB) does not release any hazardous residues into the environment. It may be produced using industries based on agricultural and hydrolyzed polysaccharide waste (Sirohi *et al.*, 2020). Agriculture waste can be used as a potential substrate for the microbial production of polyhydroxybutyrate. A variety of pretreatment procedures must be used to break down the complex chemicals in the agricultural leftovers so that PHB-producing organisms may use them as a substrate. Agro waste can be pre-treated in various ways to make simple sugars and fatty acids easily available for effective microbial consumption. For instance, it has been claimed that PHB is produced by whey, starch, oils, legumes, sugar refineries, and other lignocellulosic wastes.

It may be produced utilising a two-stage cultivation technique that includes fermentation and extraction. The separation of PHB biopolymer occurs during fermentation using carbon sources as fructose, glucose, xylose, etc (Manikandan *et al.*, 2020). The microbial strains *Bacillus megaterium*, *Cupriavidus necator*, *Ralstonia eutropha*, *Pseudomonas aeruginosa*, *Aspergillus*, *Penicillium*, etc. are some examples of those that frequently produce PHB. Due to their biodegradability, biocompatibility, and nontoxicity, PHB has several uses in nanotechnology, healthcare, the food industry, and agriculture.

Polyhydroxybutyrate and high-density polyethylene are similar in terms of their physical characteristics, such as

crystallinity, tensile strength, melting temperature, and water vapour permeability (Figure 1). PHB has excellent resistance to moisture while being stiff and rather brittle. The chiral monomer unit of PHB exhibits a high degree of polymerization and is insoluble in water. PHB is a semi-crystalline polymer whose melting properties fall between those of crystalline and amorphous materials. When pure cultures are used to make PHB, a high PHB yield of more than 80% cell dry mass is obtained (CDM). (Pradhan *et al.*, 2018)

Biosynthesis of PHB:

The biosynthetic reaction of PHB occurs only on the granule's surface. The intracellular mediation of acetyl-CoA regulates the formation of acetoacetyl-CoA reductase (Figure 2). The pool of free CoASH is increased under non-nutrient-restricted growth conditions during the exponential growth phase. However, when growth is limited by nutrients, such as phosphate or ammonium, PHB synthesis is encouraged.

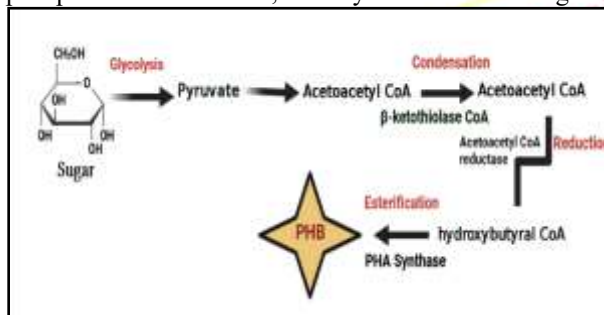


Fig.2. Biosynthesis of PHB

Industrial Production of Polyhydroxybutyrate:

PHB materials can be produced by many different bacterial strains, with reports stating that more than 300 different bacterial strains are known PHB producers. Despite these intriguing properties, industrial production of biopolymers, particularly PHB, is still in its early stages. W.R. Grace Co. of North America made the first commercial attempt to produce PHB in the 1950s. However, due to low production efficiency and a lack of a suitable purification method, this process was not successful. Polyhydroxybutyrate is available as Biomer commercially. However, commercial production was halted due to the high production costs compared to oil-derived plastics. This cost comes from the complex production process that includes several steps such as selection of the raw material, bioreaction, separation and drying of the biomass, PHB extraction, and processing. (Gast *et al.*, 2022). To commercialise PHB, significant efforts have been made to reduce production costs through the development of bacterial strains and more efficient fermentation/recovery processes (Figure 3). According to the literature, the major cost in this biopolymer production is the cost of the substrate which accounts for more than 50% of the production cost and causes the price of poly-3-hydroxybutyrate (P3HB) from Biomer to be about 12 times that of polypropylene. To address this issue, microorganisms for PHB production

are fed inexpensive substrate, renewable substrates and waste material because it provides the dual benefits of utilising waste and producing biodegradable microbial bioplastic at a low cost. (Bhuwal *et al.*, 2013)

PHB can be made by mixing different substrates under various growth circumstances, including aerobic and anaerobic growth, temperature and pH change, submerged or solid-state fermentation, and combining several substrates.

Some *Bacillus* species accumulated PHB at a rate of roughly 55.6% when utilising pre-treated sugar stick bagasse as a carbon source and 51.6% while using maize cob. When pea cell slurry (biowaste) was employed as the carbon source, PHB production was found between 945 and 1205 mg/L (55-65% w/w). A total of 435 mg/L (31-62% w/w of total cell dry weight (CDW) of PHB was produced from glucose. (Getachew and Woldensibt, 2016)

A bacterial cell's buildup of PHB is a vital survival mechanism in response to stress. Numerous bacteria have been studied for their ability to accumulate PHB, including *Bacillus cereus*, *B. subtilis*, *Alcaligenes eutrophus* [Hahn *et al.*, 1995], *Escherichia coli*, *Pseudomonas putida* [Castro *et al.*, 2013], *Rhodococcus sp. NCIMB 40126*, *Rhodococcus rhodochrous ATCC 19070* [Haywood *et al.*, 1991], *Cupriavidus necator* up to 40–50% of the dry weight of the cell is accumulated PHB. There have been reports of *Alcaligenes eutrophus* accumulating up to 96% PHB of the cell dry weight (CDW) (Anjana *et al.*, 2021).

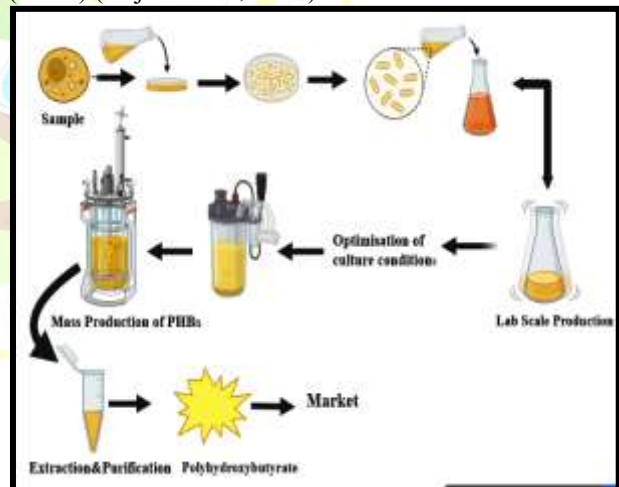


Fig.3. Industrial Production of Polyhydroxybutyrate

Different methods of PHB Extraction

One of the difficult downstream processes to make bioplastics from microorganisms is PHB extraction. There are many basic chemical extraction techniques for PHB from bacterial cell mass; they all involve three crucial steps: harvesting cell pre-treatment, polymer extraction, and post-treatment purification. Solvent extraction, chemical surfactant digestion, sodium hypochlorite, sequential surfactant hypochlorite, enzymatic digestion, and bioextraction are used to extract polymers from PHB. The yield for solvent

extraction in various strains with different solvents varied from 45 to 96%, whereas the purity of the PHB varied across procedures from 45 to 99% (for chemical digestion surfactant) and 86% to 99% (for LAS-99).

Due to its simplicity and speed, solvent extraction is a routine technique in many laboratories. PHB is dissolved in a range of organic solvents, such as 1,2-dichloroethane, chloroform, cyclohexanone, and 1,2-propylene carbonate, during the second part of the procedure. The first step entails increasing the permeability of the whole cell membrane to make PHB accessible. (Haddadi *et al.*, 2019) non-solvent precipitation in methanol and ethanol is the method used to separate the PHB solvent.

In the surfactant technique of chemical digestion, the cell membrane is damaged because the production of micelles by surfactant integration allows for the exposure of carbonosomes and the dispersion of PHBs and cell debris into the lysis solvent pool. Other techniques like sodium hypochlorite, sequential surfactant hypochlorite, and sodium bisulfite are frequently employed, although they have significant drawbacks. For example, a lower molecular weight can be produced by utilising chemical digesting surfactants such SDS, Triton X-100, betaine and sodium bisulfite.

Moreover, chemical digestion surfactant accompanied by chelate has been used to improve PHB purity. Since enzyme digestion is an environmentally friendly method with mild operating conditions for PHB recovery. Proteolytic enzymes like proteases and glycosidases have also been considered for an increase in purity without environmental drawback but with high-cost drawback and high specific activity.

The toxic reagents are needed for PHB extraction procedures such solvent extraction and chemical digestion surfactant, which also cause significant quantitative and qualitative environmental and economic losses. Biological extraction techniques are receiving increased attention for PHB extraction because of their favourable characteristics. Though these issues have not yet been resolved, they can be lessened by using more biotechnological approaches in bioextraction techniques such as the Cell engineering is often combined with the alteration of culture conditions and feedstocks in order to get around limitations of conventional approaches.

It is essential to have a firm understanding of bioextraction methods in order to build targeted green technology solutions for very pure PHB extraction with eco-friendly features. (Haddadi *et al.*, 2019)

Additionally, due to their extraction potential (especially intra-carbonosome PHB) during self-disruption and predatory digestion, bioextraction systems, including those associated with bacteriophages, predatory systems, and mealworm digestive systems, are attracting a lot of interest (Figure 4). With less detrimental effects on the environment and human health than previous methods, PHB bioextraction employing green technology may be preferred.

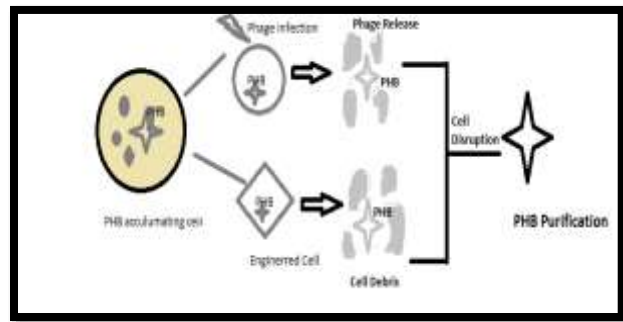


Fig.4. Bacteriophage lysis system of PHB

PHB based biocomposites:

By overcoming its inherent constraints, the creation of biodegradable PHB-based biocomposites with enhanced mechanical qualities might lead to the opening of new doors for industrial applications. As a result, nanotechnology is a very promising area of research for the twenty-first century and is essential for the extensive rebuilding of novel applications in the field of biotechnology. (Pande and Sanklecha, 2017). The modernization, creation of more ecofriendly products, and development of more effective procedures have greatly improved today's quality of life. Exploiting resources that are sustainable and renewable is necessary to fight this expanding tendency. It is a simple, cost-effective, and environmentally friendly process to produce gold, silver, and platinum metal nanoparticles by microbial synthesis. (Kavitha *et al.*, 2018) Based on a number of factors, green technology produces nanoparticles that are much better than those made through physical and chemical processes. Green methods, for instance, don't utilise costly chemicals, use less energy, and create products and byproducts that are safe for the environment. (Patra and Beck, 2014) PHA's structural characteristics enable the creation of nano-sized PHA pellets that come in a variety of forms and sizes. This opportunity expands the potential applications for PHA as a nanocomposite. Another type of materials known as bionanocomposites are nanocomposites made of naturally occurring polymers (biopolymers) combined with inorganic nanoentities (BNCs). Compression, extrusion, moulding, and injection are some of the several processes used to create biocomposites. (Raza *et al.*, 2019) Their nanocomposites were designed to increase the PHB's toughness. According to studies, PHB nanocomposites of various compositions shown improved physical characteristics with an increase in the rate of elongation range of roughly 5-80% as comparison to 2% for neat PHB. (Kavitha *et al.*, 2018)

An efficient method for producing biopolymers with enhanced characteristics is the mixing of PHA polymers. The parent polymer's limits are restricted by blending. PHB blends have drawn interest because they improve the physical and mechanical characteristics of PHBs. PHBs mix with organic polymers including starch, cellulose, and lignin. (Tripathi *et al.*, 2021). Therefore,

PHB must be combined with other substances or biopolymers to produce new PHB-based biocomposites with added value. PHB has been incorporated with different biomaterials (or biopolymers) several times in an effort to create sustainable biocomposites. For instance, PHB's brittleness is reduced by combining it with other substances to create unique biocomposites including PHB/poly (ethylene glycol) (PEG), PHB/cellulose, PHB/starch, and PHB/chitosan. Novel biocomposites should be tangible to a variety of forms, including particles, fibres, mouldings, films, membranes, foams, and coatings. (Raza *et al.*, 2019)

PHB/cellulose: In order to retain the crystalline character of cellulose fibres, the structure of cellulose comprises hydroxyl groups for inter and intra hydrogen bonding between glucopyranose units. (Raza *et al.*, 2019) PHBs are incorporated with appealing polymers called cellulose derivatives. For instance, cellulose propionate, cellulose acetate butyrate, and ethylcellulose are frequently utilised as a PHB blend. (Tripathi *et al.*, 2019). Cellulose derivatives help PHB break down and are compatible with it. Hydrogen bonding within the cellulose molecules is what gives the material its high modulus (138 GPa) and tensile strength (18GPa). These characteristics allow for the incorporation of cellulose into PHB to create biocomposite materials. (Raza *et al.*, 2019) Wei and colleagues (2015) used a dicumyl peroxide-based extrusion technique to graft PHB onto the cellulose fibres. Efficiency of grafting was influenced by concentration and reaction time. The degree of crystallinity was decreased in both the amorphous and crystalline portions of the PHB and cellulose as a result of the grafting mechanism. Smaller PHB crystals also decreased the brittleness of the material. PHB and cellulose grafted copolymers were more stable than ungrafted PHB and cellulose. The created bio-composite could be applied to packaging and other things. To create a bionanocomposite based on PHB and cellulose nanocrystals, Seoane and colleagues (2015) employed the solution casting method (CNCs). They noticed that CNCs in the PHB matrix have the best features for nucleation. According to the study, as CNC concentration increased, so did Young's modulus and tensile strength. When compared to pure PHB, the produced bionanocomposites showed reduced water vapour permeability, and they also showed better UV barrier characteristics (propylene). Potential uses for the created composite include packaging. In a different work, Seoane et al. (2016) used solvent casting and compression moulding to create biodegradable bilayer composites based on PHB and cellulose cardboard. Due to the hydrophobic PHB solution penetrating the hydrophilic cellulose cardboard fibres, compression moulded composites experienced more moisture absorption than composites created using the solvent casting approach. As a continuous layer of PHB was generated on the composites created by compression moulding, they showed better mechanical characteristics than the composites created by solvent casting made of

cellulose, cardboard. Due to the hydrophobic PHB solution penetrating the hydrophilic cellulose cardboard fibres, compression moulded composites experienced more moisture absorption than composites prepared using the solvent casting approach. As a continuous layer of PHB was generated on the cellulose-based cardboard, the composites created by compression moulding displayed better mechanical characteristics than those created using solvent casting. The produced composites were used in the agriculture and food packaging industries.

PHB/Starch: Since starch is naturally biodegradable, it is frequently utilized as a natural polymer. Because PHB is compatible with starch, production costs are reduced and the product's qualities are improved. The PHB-starch mixture had a single glass transition temperature and a 30:70% higher tensile strength than PHB. (Tripathi *et al.*, 2021). The food packaging industry can use this mixed PHB film as a coating material. PHB-based starch biocomposites had been developed using a variety of methods. The methods being thought about enhanced the thermal and mechanical characteristics of PHB, which encouraged totally biodegradable composites. Through the use of the melt compounding approach, Zhang and Thomas (2009) created composite blends of starch and PHB that included the two substances in a 70:30 weight percent ratio. They noticed that hydrogen bonds formed between the carbonyl group of PHB and the hydroxyl group of starch, preventing PHB's chain scission degradation and enhancing the composite's temperature stability. Melt mixing and heat pressing were used to create PHB-based starch composites, according to Lai, 1995 and colleagues (2006). After adding water and glycerol as plasticizers, the starch granules were distributed throughout the PHB matrix using the gelatinization process. According to the study, increasing glycerol level boosted weight loss and water absorption, but increasing PHB content had the opposite effect. In a mix of soluble potato starch and PHB, they found that weight loss and water absorption were 30.3% and 70.9%, respectively.

PHB/ Hydroxyapatite: Wet chemical precipitation, biomimetic deposition, or electrodeposition are all ways to make HA. Calcium phosphate, which has strong osteoconductivity, bioactivity, biocompatibility, high stiffness, and low elasticity, forms the basis of the HA structure. Some HA mediated PHB composites had been produced for dental and orthopaedic implants in order to enhance their mechanical properties. Using compression moulding, Shishatskaya et al. (2006) created a hybrid composite made of PHB and HA. Surface wettability, interface energy, and cohesive forces all improved as HA content in the composites increased. According to Zhuo et al. (2010) HA and PHB were created using hot pressing and ball milling. By utilising silane as a coupling agent to form covalent bonds with both the HA and the PHB, the interface of the HA/PHB composite was enhanced. The developed biocomposite might be

employed in bone tissue engineering as a fracture fixation material.

PHB/Chitosan: Chitin, the main component of crustacean aquatic creatures' exoskeletons, is deacetylated to produce chitosan, a cationic polysaccharide. Since chitosan has so many desirable qualities, including reactivity, biodegradability, natural origin, and availability, it may be used in a wide range of industries, including waste and water treatment, medicine, biotechnology, and manufacturing. (Saini *et al.*, 2017) By using the precipitation process, Chen *et al.* (2020) created the composite consisting of chitosan, PHB, and maleated PHB. Crystallinity, T_m , and H_m of the produced composite reduced when chitosan content was increased. The PHB/chitosan (80:20) composite had T_m and H_m values of 171.6 C and 87.1 J/g on DSC analysis, as opposed to the maleated PHB/chitosan composite. Emulsion-blending and porous PHB/chitosan scaffolds were created by Cao *et al.* (2005) using PHB/chitosan composite films. When PHB concentration was increased, the elastic modulus and swelling capacity of the films reduced from 141.1±5.9 to 119.3±4.3% and 8.7 ± 1.6 to 4.9 ± 0.6 MPa, respectively. The study found that when compared to native chitosan films, PHB/chitosan films had a lower elastic modulus but a greater tensile strength.

Starch, cellulose, chitosan, and HA are the most crucial chemical moieties to make biocomposite with PHB for potential relevance in food packaging and biomedical applications, it can be concluded after studying all of the aforementioned biocomposites (Table 1)

Table 1. lists various techniques for creating nanocomposite for usage in the food and healthcare industries.

Nanocomposite	Method of fabrication	Obtained characteristics	Applications
PHB/Cellulose	Extrusion based graft technique	Lessen brittleness and crystallization	Food Packaging
PHB/CNCs	Casting Solution	Increased Tensile strength and Young's Modulus	Food Packaging
PHB/Hydroxy apatite	Compression moulding	Lower decomposition temperature, Higher crystallinity	Artificial Bone tissue
PHB/Starch	Melt compounding	Thermal stability high	Packaging
PHB/Chitosan	Precipitation Technique	Increased T_m and H_m	Tissue engineering

Applications of PHB based composite

Nanocomposites have several advantages, including cheap cost, high accessibility, ease of fabrication, low density, high transparency, good flow, improved surface characteristics, and flammability resistance. (Motaung *et al.*, 2018) Because of their unique qualities, these

materials have drawn the attention of both industrial and educational institutions, including medical, cosmetics, agriculture, and food sectors. Recent developments in PHB-based composites open up new possibilities for applications in health, food packaging, and agriculture.

Agriculture:

To maintain healthy soil structure, moisture retention, and weed control, mulching is a crucial agricultural technique. The mulch films were created using Mirel™ PHB and Nodax™ P(3HB-co-3HHx) (Boey *et al.*, 2021). Due to the demand for eco-friendly materials, the depletion of natural resources, and increased awareness of environmental issues, agricultural biomass products are increasingly being used and applied in the development of polymer nanocomposites. Smart polymeric systems have significantly benefited the agricultural industry by improving the efficacy of pesticides, herbicides, and fertilisers by supporting controlled release systems and so enabling the use of lower dosages. (Sikder *et al.*, 2021) A sustainable agriculture delivery system should include the following desirable characteristics:

regulate agrochemical release at the appropriate dose, safeguard the agrochemical from deteriorating conditions such as light and pH.

have lower cytotoxicity than traditional insecticides the nanocarriers' long-term validity, which will lower the frequency of pesticide application and treatment by increasing their lifetime.

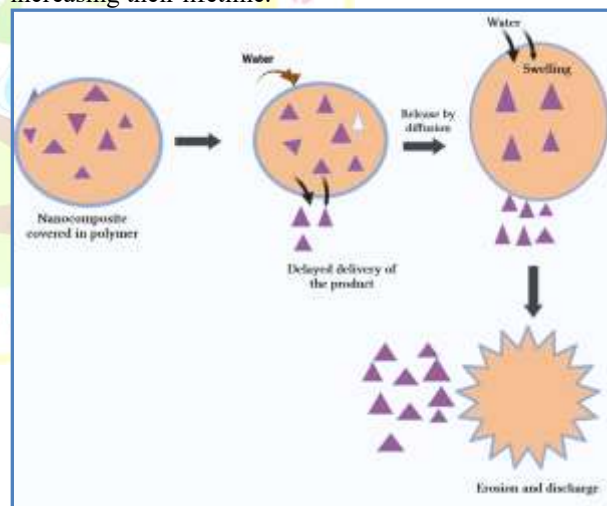


Fig 5. Nanocomposites made of polymers that, by absorbing water, encourage the gradual release of agricultural chemicals

When these ENC (engineered nanocomposites) are dissolved in a solution, nutrients may be readily released from them in the form of soluble ions. In order to create effective nanoencapsulated techniques, it is possible to administer the nutrient components in a way that results in an encapsulated nanofertilizer that is specifically designed for controlled release. A number of factors, such as particle size, distribution, solubility, shape,

surface area, encapsulation mechanism, and release mechanism, should be carefully taken into account. Emulsification, coagulation, inclusion complexation, solvent displacement or nanoprecipitation, are some of the most frequently utilised nanoencapsulation processes. Along the use of fluorescently tagged nanocarriers for the transport and release of agrochemicals, Liu et al. (2015) have made it possible to easily trace chemicals through the food chain using an easy fluorescence detection system. They have created a special pesticide nanocarrier that utilises water-soluble cationic dendrimers. Its structure includes a core made of fluorescent perylene diimide (PDI), which is coupled to hydrophobic polyesters and periphery amino acids. (Sikdar et al., 2021).

Herbicide was combined with natural-synthetic PLA/PBAT polymers by Akhir and Mustapha (2022) in order to limit weed growth. A melt transesterification was used to create 2-methyl-4-chlorophenoxyacetic acid (MCPA) conjugated with poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). In order to create biodegradable mulch film with the addition of slow-release herbicides, the resulting bioactive oligomer herbicide was combined with PLA/PBAT (30/70).

Jayakumar et al. (2022) used cheese whey permeate as a substrate for *Bacillus megaterium* to synthesis and analyse the PHB-silver bionanocomposite (PHB-AgNc). TEM, SEM, FTIR, and NMR were used to characterise the extracted PHB-AgNc. High antimicrobial resistance is demonstrated by PHB-silver bionanocomposite against *E. coli* and *Pseudomonas* spp. A 96-hour batch fermentation experiment was conducted in a 14 L bioreactor. The greatest yields for both biomass and nanocomposite were 5.8 and 2.4 g/L, respectively.

Food packaging

As a result of substituting traditional plastic materials, PHB-based biocomposites have superior gas barrier qualities for packaging applications. This increase in demand is a result of rising environmental worries over the widespread use of synthetic, non-biodegradable polymeric packaging, namely polyethylene. The primary purpose of food packaging is to protect food products from microbial deterioration, toxic pollutants, oxygen, moisture, light, external force, etc. during storage and transit as well as to extend the shelf life of the food product. (Joseph et al., 2020) Environmentally friendly packaging made from naturally occurring polymers like Polylactide, PHB, and chitosan—which is particularly effective in food packaging—has been produced more often in recent years. Bioactive agents can be added directly to packing compounds to create antimicrobial packaging, coated on the surface of packaging to create antimicrobial packaging, or formed into films using antimicrobial polymers. (Jose et al., 2020) PHB, PLA, and starch and their derivatives have several properties that make them suitable with a variety of antimicrobial agents for packaging.

Vanillin, sophorolipid, and eugenol are a few examples of natural antimicrobials that were added to PHB-based biomaterials at various doses for active packaging materials. In a study, Zhong and his colleagues (2020) discovered that PHB films containing vanillin and eugenol, even at tiny amounts (80 g/g PHB), were effective against several bacterial species. Furthermore, adding these organic antimicrobials to PHB typically causes the films' thermal stability and mechanical qualities to decline.

Graphene nanoplatelets (GNPs) were used in the manufacturing of PHB-based film, according to Manikandan et al. (2020) as evidenced by the reduction of roughly 56.92% for WVP compared to the pristine film ($1.50 \times 10^{-10} \text{ gm}^{-1} \text{ h}^{-1} \text{ Pa}^{-1}$ WVP), they claimed that the addition of 0.7 weight percent GNP to PHB film showed the greatest barrier qualities. By forming a tortuous structure inside the matrix, impermeable GNP might be inserted, which would minimise permeability. These findings were directly connected to the longer shelf lives of milk and potato chips, which were 245 days and 26 days, respectively, as opposed to 60 days and 6 days for the control.

Alim et al. (2022) evaluated the modification of PHB film with thermoplastic starch (TPS), organically modified montmorillonite (OMMT), and eugenol (Eug). The thermal stability study revealed that the additives' presence had no appreciable impact on the degradation temperature of PHB film (T_d : 299.20 °C). Additionally, when OMMT was added, the modulus increased by 12.82% compared to pure PHB, while it fell by 24.68% for the PHB/TPS film (1560 MPa).

Table 2. Biopolymer blended with nanoparticles shows antimicrobial activity

Nanoparticles	Biopolymer	Antimicrobial activity	Application
Ag	Chitosan	<i>E. coli</i> , <i>S. aureus</i> , <i>A. niger</i> , and <i>P. citrinum</i>	Active food packaging for litchi fruits
Ag	Nanostructured starch	<i>S. aureus</i> , <i>E. coli</i> , and <i>C. albicans</i>	Active food packaging
CuS	Agar	<i>E. coli</i> and <i>L. monocytogenes</i>	Active food packaging
ZnO	Ethyl cellulose	<i>E. coli</i> and <i>S. aureus</i>	Active food packaging
Silica	Chitosan	<i>E. coli</i> , <i>S. typhimurium</i> , <i>S. aureus</i> , <i>L. monocytogenes</i>	Active food packaging
TiO ₂	Wheat gluten and cellulose nanocrystals	<i>S. cerevisiae</i> , <i>E. coli</i> , and <i>S. aureus</i>	Active food packaging

Source: (Omerovic et al., 2021)

Recent investigations on composite films used to preserve bread for longer periods of time and using apricot kernel oil revealed total fungal growth inhibition (Guminnea *et al.*,2021). The antibacterial chemicals released by the active films developed by solvent casting were effective against the target microorganisms (Zhong *et al.*,2020). Fruit that has been coated with an edible substance aid in enhanced product stability and quality preservation (José *et al.*,2020). Applications of biocomposites should go beyond only packaging materials and include the development of biosensors that can quickly identify defective or tainted food, the presence of bacteria, and other things. (Joseph *et al.*,2020) Table 2.

Medical:

Due to their excellent biodegradability and biocompatibility, PHB-based biocomposites may have biological applications. In PHB's stereochemical regularity and a degree of crystallinity of 60–80%, which only use it in the biomedical field. (Raza *et al.*,2019) PEG-PHB-folic acid nanoparticle composite are created using the solvent evaporation method for oil/water emulsions. The medication paclitaxel was added to the produced nanoparticles. Results revealed that nanoparticles contained little amounts of drugs. It had a uniform distribution and little agglomeration. (Rezaei *et al.*, 2016)

Electrospinning and electrospaying were used to create PHB-based biocomposites scaffolds for PHB/HA (Koller *et al.*,2018). Naveen *et al.* (2020) successfully applied an electrospinning approach to produce PHB nanofibrous drug carriers using hexafluoroisopropanol (HFIP) as the solvent. These nanofibrous scaffolds displayed supported fast cell growth without negatively effecting cellular morphology; a cell viability of 87% was attained after 48 h.

By electrospinning thin films of P3HB-nHA, Chen *et al.* (2017) were able to observe that bone marrow mesenchymal stem cells had more favourable adhesion, proliferation, and osteogenic characteristics than P3HB-only cells did. Based on P3HB and HA, Degli Esposti *et al.* (2019) created bioactive and biodegradable porous scaffolds for bone tissue regeneration. In order to repair significant radial parietal bone lesions in rats, Ielo *et al.*(2022) examined the osteogenic potential of hybrid composite P3HB-Alg-HA scaffolds on mesenchymal stem cells (MSCs) Biocomposites including PHB and PHV sutures for biomedical applications and PHB composites containing HA for bone tissue engineering have both been produced using this material extensively. PHB/cellulose, PHB/chitosan, PHB/PEG, and PHB/HA composites all had improved thermal and mechanical properties.

CONCLUSION

The development of renewable feedstocks that are not sources of food or feed has been sparked by the present trends and difficulties in industrial biotechnology with regard to sustainability. Bioplastics have drawn a lot of

interest in recent years from academic and industry researchers among the many green goods that are now on the market. PHB is the highest performing biopolymer currently on the market, and its widespread use would significantly ease the strain on the finite supplies of fossil fuels. However, the high cost of PHB production prevents the PHB production technique from being really commercial. For example, building up effective aerobic fermentation facilities and purchasing diverse feedstocks and organic solvents for polymer extraction both come at a significant capital cost. Due to this biopolymer's fundamental characteristics of biodegradability and biocompatibility, it is now possible to see it being widely used as a drug carrier in the biomedical area, as a nanoencapsulation of agrochemical in agriculture, as a biocomposite in nanotechnology, and in the food business. Biocomposites are made by mixing inorganic nanoparticles with biofilm-forming elements such polysaccharides, proteins, and nucleic acids. Agriculture, food packaging, pharmaceuticals, biosensors, and biofuels all make extensive use of biocomposites. In this overview, several recent developments in the design of agrochemical-controlled release systems are highlighted. It is obvious that using controlled release devices to apply agrochemicals can lower the total use of pesticides and commercial fertilisers. The excellent potential of biodegradable films made of nanomaterials for active packaging increases shelf life and preserves or enhances the quality of packaged goods.

Future Outlook:

The use of PHB and related composites as packaging materials, controlled-release delivery systems, and medication carriers has a lot of potential. PHB has a wide range of claimed commercial uses, from packaging to biological applications. PHB biocomposite may be created using a variety of techniques, but electrospinning has emerged as the most promising. There are several ways to PHB is more suited for usage as scaffolds after plasma treatment because it can encourage compatibilization between hydrophilic fibres and hydrophobic matrix through free radicals and surface cross-linking. As they provide for the best quality and safety of food, active antimicrobial packaging is a novel idea in food packaging that is attracting interest among researchers as well as among manufacturers and representatives of the packaging sector. Therefore, future research should concentrate on avoiding tying antimicrobial effects to the rate of microbial growth in packaged foods using both industrial and laboratory methods. This will aid in the early development of packaging that is resistant to microbes. Synergy, nanocomposites, and blending are examples of antimicrobial performance improvement tactics that will be essential tools to improve antimicrobial packaging and get around some operating restrictions. Despite the fact that bio-nanomaterials have many benefits, there is still much to be done to adapt these materials. Nanomaterials can't be commercialised because of

technical issues including incompatibility, uneven dispersion, and poor surface adhesion between them and substrates. To have a more sustainable method of obtaining ecologically acceptable biomaterials that are superior candidates for next-generation multi-modified biofilms, these problems still need to be solved.

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