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# SIGNIFICANCE OF POLYHYDROXYALKANOATES AMIDST COVID-19: A COMPARATIVE REVIEW

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## ABSTRACT

Polyhydroxyalkanoates (PHA) are biodegradable polymers which are the need of the hour. Due to the Covid-19 pandemic, we witnessed an exponential increase in the use and disposal of single use plastic The increase can be attributed to the lockdown measures and other efforts for mitigating the viral infection. PHAs are bacterial polymers which accumulate in the bacterial cell facing stress conditions. This polymer is non-toxic, biodegradable, biocompatible, has high tensile strength and good gas barrier properties. These properties allow the application of this polymer in various different industries, thus, making this polymer industrially relevant. In this review, we summarize the need and the properties of PHA. Further, we briefly discuss and compare PHA to other biopolymers and synthetic plastics. Ultimately, we summarize the cost-effective substrates utilized for the production of PHA; promoting a circular, green economy. Thus, in this review, we outline the significance of PHA as an alternative to petrochemical-based plastics, in the current world scenario.

**Keywords: Polyhydroxyalkanoates; Biodegradable; Synthetic plastics; Bioplastics; PHA**

## INTRODUCTION

In the year 2020, we witnessed the worldwide spread of infections caused due to the novel SARS-CoV-2. The immediate method of mitigating the spread of the virus involved the utilization of single-use personal protective equipment (PPE) including gloves, surgical face masks, face shields, protective eye glasses, coveralls and respirators. Further, a surge in the demand for hand sanitizers, cleaning agents and packaging material was also observed **[1]**. To meet this demand, the exponential increase in the manufacturing, use and disposal of these plastic-based products is adding significantly to the existing environmental stress.

Eco-friendly biopolymers are the need of the hour to support sustainability for the decades to come as an alternative to petrochemical-based plastics. Efficient technologies are being developed that utilize renewable resources for the production of these bioplastics while conserving natural ecosystems **[2]**

Bioplastics are biobased, biodegradable (or both) materials which have found applications in industries like packaging, electronics, automotive and agriculture etc. as an alternative to non-degradable plastics **[3]**. Bioplastics which are biobased and biodegradable are gaining more interest as they can be derived from renewable resources and also can decompose naturally in the environment or can be turned into compost **[4]**. Bioplastics like Polyhydroxyalkanoates (PHA), Polylactic acid (PLA), Thermoplastic starch (TPS) and Regenerated cellulose fall under this category.

In this review we compare the different types of bioplastics and compare the properties of PHA to different synthetic plastics. We highlight the properties and importance of PHA and the cost-effective substrates commonly used for PHA production.

## PHA VS OTHER BIOPOLYMER

The annual world plastic demand currently stands at more than 360 million tons, this demand has increased in the past five years from 300 million tons. Out of the 360 million tons plastic produced, only 9% accounts for reusable plastics. (https://www.theweek.in/news/sci-tech/2020/09/21/Global-plastic-production-up-by-60-MMT-in-5-years-Researcher.html#:~:text=Speaking%20on%20Microplastics%3A%20An%20emerging,to%20360%20million%20metric%20tonnes.%22). Despite the growing environmental concerns and hazards of the discarded single-use plastics, bioplastics form less than 1% of the total plastic produced **[5]**. The most popular bioplastics in the market are made from starch (from corn) and cellulose (from sugarcane).

PLA is a common bioplastic made from polylactides and is being used to make oxo biodegradable plastic bags. PLA comes from a family of aliphatic polyesters which are synthesized as a result of a multistep process. It initiates by the production of lactic acid followed by the formation of lactides leading to its polymerization; resulting in PLA. Lactic acid is produced by bacterial fermentation of carbohydrates, PLA is then produced by chemical condensation **[6]**. The Global PLA market currently stands at 535.6 million dollars and is expected to annually rise by 15.9% upto 2027. Though the Covid-19 pandemic has led to a decline in the direct demand for PLA but it is forecasted that PLA demand could increase in the textile industry for use in PPEs used to tackle Covid 19. (https://www.grandviewresearch.com/industry-analysis/polylactic-acid-pla-market)

The major advantages of the PLA plastics can be attributed to its biodegradability, thermoplastic nature, rigidity and stability **[7]**.

Similarly, botanical starch obtained from plants such as pea, potato, maize, barley, wheat and rice can be used to make TPS. It is developed by thermomechanical processing of granular starch, the processing can be done by processes like kneading, extrusion, injection moulding, compression moulding and blow moulding. Additionally, TPS can also be obtained by adding water soluble plasticizers to aqueous dispersions containing starch **[8]**. TPS find various applications as bioplastics because it is renewable in nature, biodegradable and can be used as fertilizer upon degradation. Further, it is cheap, abundant in nature and can be easily processed by standard equipment due to its flexible nature **[9]**. Yet, TPS is not a suitable replacement for petrochemical based plastics due to its hydrophilicity, poor mechanical properties. Above the threshold Tg value, the bioplastic loses its mechanical properties and swells irreversibly. Thus, TPS needs to be blended with other materials to obtained a bioplastic suitable for various commercial applications **[10]**.

Cellulose is a common naturally derived polymer found in various plants. It is renewable, easily available, biodegradable, low cost and non-toxic. Cellulose can be regenerated to improve its tensile strength by treating it with solvents. The regenerated cellulose overcomes the drawbacks of natural cellulose i.e. strong hydrogen bonds between molecules within cellulose in turn makes it difficult to dissolve and process for industrial applications **[11]**. On the contrary, the processing itself requires high mechanical energy, high operational costs, expensive chemicals and pressurized reactors **[12]** .

PLA, TPS and Cellulose-based bioplastics are competitively priced and have similar properties to petrochemical-based plastics. Yet, they may not be a sustainable alternative to the non-degrading plastics. If feedstock like corn and sugarcane are utilized for bioplastic production, it competes with the raw material as food for humans and other animals **[13]**. Additionally, since harvestable land and raw feedstock are limited in nature, it is not feasible to repurpose these materials to produce bioplastics which are only compostable and not biodegradable. Further as the demand for the crop-based bioplastics increases, it leads to an increase in the harvest of the crops and ultimately adding to the increased Greenhouse Gas emissions **[14]**.

Thus, the attention is now on PHA, these bioderived, natural polymers are biodegradable in nature and don't use renewable feedstock as raw material. Bacterial systems are most commonly used for industrial production of PHA. These systems are renewable in nature, do not compete with any feedstock and also use waste material as substrates **[15]**. Further, PHA is synthesized by microbial fermentation while the other biopolymers require chemical synthesis routes.

PHAs are bioderived, natural polymers which are biodegradable in nature and their properties are comparable to that of fossil-fuel based plastics. This polymer accumulates in the bacterial cell as an energy reserve for the bacteria when facing nutrient limiting conditions with excess of carbon.The polymer is non-toxic, biocompatible, biodegradable and has properties similar to that of petrochemical based plastic **[16]**. More than 150 monomers of PHA have been identified with properties which range from thermoplastics to elastomers. Thus, the differing monomers are organized as homopolymers or heteropolymers based on the substrate provided to the bacteria **[17]**. These PHA polymers find application in various industries based on their properties: pharmaceutical and therapeutic applications **[17]**, packaging applications **[18]** , Medical applications **[19]**, drug delivery and tissue engineering **[20]** etc.

**PHA VS SYNTHETIC PLASTICS**

Personal Protective Equipment (PPE) employed in Covid-19 pandemic, is made up of different synthetic plastics like polypropylene (PP), polystyrene (PS) and polyethylene (PE). Further, the lockdown lead to an increase usage of packaging material for food and essential deliveries; adding to the plastic waste generation **[21]**.

Common synthetic plastics which are used as packaging material or as single use plastics during the pandemic are:

- Polyethylene (PE) - used to make packaging films, trash bags, grocery bags and other commonly used plastic products.
- Polypropylene (PP) – used to make PPE kits including goggles, shoe covers, face masks, gloves, coveralls, head covers and face

shields. Further, COVID-19 test kits are predominantly made of PP along with other medical devices like injections etc. It is also used to make rigid and flexible packaging material.

- Polystyrene (PS) - used to make hospital ventilators, food and packaging materials.

To circumvent the severe problems caused by the disposal of these plastics, different kinds of PHAs are being used as appropriate substitutes for PS, PP and PE **[22]**. **Table 1** depicts the properties of different polymers and demonstrates that PHA is a polymer of biological origin which is biodegradable and has a vast range of properties which can align with the properties of petrochemical - based plastics and further, can be altered based on the required application. The properties of the polymer vary with its different monomer composition. The composition is dependent on two main variables – the bacteria used and the carbon provided to the bacteria in the growth medium.

## PHA PRODUCTION USING COST-EFFECTIVE SUBSTRATES

The carbon source is an important factor for maintaining polymer composition and to control the cost of production. It is estimated an approximate 50% of the cost can be attributed to the raw materials used in the production process. In an effort to make PHA commercially viable and a suitable alternative for synthetic plastics, various studies are being carried out to reduce the cost of PHA production. Thus, researchers have utilized different cost-effective substrates as an alternative to glucose and other carbon sources **(Table 1)**. Different bacteria capable of metabolizing the different complex substrates are employed in these studies. For instance, Kovalcik *et al*. demonstrate the utilization of grape winery waste as a substrate for PHA production. They observed a change in the average molecular weight in the polymer with the change in the type and amount of carbon. PHA accumulation of 76.8% was observed when using grape oil as a substrate, Further, PHA with high molecular weight was obtained when using grape sugar extract as a substrate. Different bacterial strains were employed for each waste resulting in polymers with different properties **[23]**. Alternatively, Aljuraifani *et al*. demonstrate how the same bacterial strain can be used to metabolise three different wastes i.e. rice bran, soy molasses and date molasses. Varying PHA accumulation was observed in the *Pseudomonas sp.* when it was grown in different substrates **[24]**. Halophilic bacteria have also been employed to metabolize substrates like pomegranate peels (*Bacillus halotolerans)* **[25]**, waste frying oil (*Halomonas hydrothermalis)* **[26]**, grape sugar extract (*Halomonas. Halophila)* **[23]** etc. **Table 2** summarizes recent research being carried out PHA production using cost effective substrates. Thus, the usage of these cost-effective substrates not only reduces the waste disposal of these substrates but also promotes a circular, green economy.

**Table 1: Comparison of properties: Polyhydroxyalkanoates (PHA) against polystyrene (PS), polypropylene (PP) and polyethylene (PE)**

| | Biodegradable | Compostable | Biocompatible | Recyclable | Polymerisation | MW X$10^4$ | $T_m$ | Mechanical properties | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | °C | YM (Mpa) | EB (%) | TS (Mpa) |
| PHA | Yes | Yes | Yes | N.A. | Biological | 30-100 | 60-170 | 10-1000 | 1-1000 | 1-45 |
| PS | No | No | Yes | No | Chemical | 10-40 | 270 | 3000-3600 | 3-4 | 46-60 |
| PP | No | No | Yes | Yes | Chemical | - | 130-170 | 1300-1800 | 100-300 | 25-40 |
| PE | No | No | Yes | Yes | Chemical | - | 115-135 | 800 | 500 | 22-31 |

MW- Molecular weight x ($10^4$); $T_m$ – Melting temperature; YM – Young's Modulus; EB- Elongation break; TS- Tensile strength

**Table 2: Summarising cost effective substrates used for the production of PHA along with the microorganisms used and PHA yield**

| Substrate used | Microorganisms used | PHA type | PHA yield | Reference |
|---|---|---|---|---|
| Molasses | *Cupriavidus necator* | PHB | 64.32% | [27] |
| Cheese whey | | PHB | 64.29% | |
| Corn husk | *Bacillus megaterium* | PHB | 57.80% | [28] |
| Glycerol | *Zobellella denitrificans* | PHB | 85% | [29] |
| Cane molasses | *Alcaligenes sp* | PHB | 79.26% | [30] |
| Waste frying oil | *Halomonas hydrothermalis* | PHB | 61.98% | [26] |
| Pomegranate peels | *Bacillus halotolerans* | PHA | 83% | [25] |
| Tuna condensate waste | *Cupriavidus necator* | PHB-HV | 50.7% | [31] |
| Date molasses | *Pseudomonas sp* | PHA | 82.6% | [24] |
| Rice bran | | PHA | 90.9% | |
| Soy molasses | | PHA | 91.6% | |
| Cashew apple juice | *Cupriavidus necator* | PHB-HV | 15.78 g/L | [32] |
| Grape oil | *Cupriavidus necator* | PHB | 76.8 % | [23] |
| Grape sugar extract | *Halomonas. halophila* | PHB | 57.0% | |

## CONCLUSION

In a world that requires drastic decline in the use and discard of non-biodegradable plastics and sustainable use of resources, PHAs can be considered as plastics the way nature intended plastics to be. PHAs are bioderived, natural polymers which are biodegradable in nature and their properties are comparable to that of fossil-fuel based plastics. The properties of this polymer are similar to that of synthetic plastics and thus, can be used as a green alternative to the non-degradable plastic. Thus, the manufacturing and application of PHAs need to be increased exponentially in order to meet with the plastic demands; already overburdened by the Covid-19 pandemic.

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