International Biodeterioration & Biodegradation 126 (2018) 45–56

Contents lists available at ScienceDirect

International Biodeterioration & Biodegradation

journal homepage: www.elsevier.com/locate/ibiod

Review

Polyhydroxyalkanoates: Characteristics, production, recent developments and applications

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ARTICLE INFO

Keywords:
Polyhydroxyalkanoates
Biopolyester
Bioplastic
Nanotechnology
Polyester

ABSTRACT

Polyhydroxyalkanoates (PHAs) are biopolyesters, stored within cells as energy storage materials by various microorganisms. Due to their biocompatibility and biodegradability, PHAs have a wide range of applications in various industries such as biomedical sector including tissue engineering, bio-implant patches, drug delivery, surgery and wound dressing. PHAs are green plastics and they have positive social and environmental impact when compared with conventional plastics in terms of production and recycling. Moreover, PHAs do not possess acute and chronic health effects when used *in vivo*. These bioplastics represent a renewable and sustainable resource to reduce landfill requirements without being persistence or causing pollution. A wide range of carbon sources, bacterial strains, fermentation conditions and recovery methods have been purposed by various researchers for better yield and economical perspectives. Recent advancements in synthetic biology and genetic engineering has led to the production of PHAs from non-PHAs producing strains with no toxins. Progression in recovery techniques has improved the extraction efficacy from biomass with high purity. This review outlines production and characteristics of PHAs, developments in their production, and applications in various industries including nanotechnology.

1. Introduction

The production of petroleum based plastics has a big disadvantage of generating non-degradable waste products (Akaraonye et al., 2010). The non-biodegradable nature of these products, due to their high molecular mass and complex structure imparts a high environmental burden as they can remain in water bodies, soil and landfill for many years. Concerns over the harmful effects of these petrochemical derived plastics by public and environmental bodies have been increased. This awareness prompted a global scientific drive to develop alternative green, ecofriendly and biodegradable polyesters and plastics substitutes.

The term "polyester" refers to polymers containing ester groups in their molecular chains. Microbial fermentation produces polymeric materials with the most common building blocks as shown in Fig. 1. Except polyhydroxyalkanoates, which is carried out *in vivo*, all other polymers are polymerized *in vitro* by chemical reactions (Chen, 2010).

2. Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are bio-polymers, synthesized by microorganisms as lipid inclusions for energy storage in granular forms within the cellular structure (Poli et al., 2011). The French scientist Lemoigne first discovered PHA in *Bacillus megaterium* in the form of poly (3-hydroxybutyrate) (PHB) in 1925 (Chee et al., 2010). PHAs are natural polyesters of 3-, 4-, 5-, and 6-hydroxyalknoic acids which are thermoplastics. To date, more than 90 genera of both Gram-positive and Gram-negative bacteria have been identified as PHAs producers under both aerobic and anaerobic conditions (Kim et al., 2007; Zinn et al., 2001). Many microorganisms can store intracellular inorganic and/or organic inclusions which are surrounded by phospholipids. For instance, if the inclusion has an iron oxide core, it is called inorganic inclusion like magnetosomes; while, if the inclusion has a polyester core, it is called organic inclusion such as PHAs (Poli et al., 2011; Rehm, 2007). In the case of PHAs, the core of polyester is surrounded by either phospholipids or proteins. Bacteria store PHAs within the cytoplasm where PHAs exist as granules ranging in size from 0.2 to 0.5 μm.

Bacteria can be divided into two groups with regards to PHAs production. In the first group, bacteria requiring limitation of a nutrient such as phosphorous, nitrogen, oxygen or magnesium to accumulate PHAs and they do not accumulate PHAs during the growth phase. The second group accumulates PHAs during the growth phase and do not

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http://dx.doi.org/10.1016/j.ibiod.2017.10.001
Received 4 January 2017; Received in revised form 15 September 2017; Accepted 4 October 2017

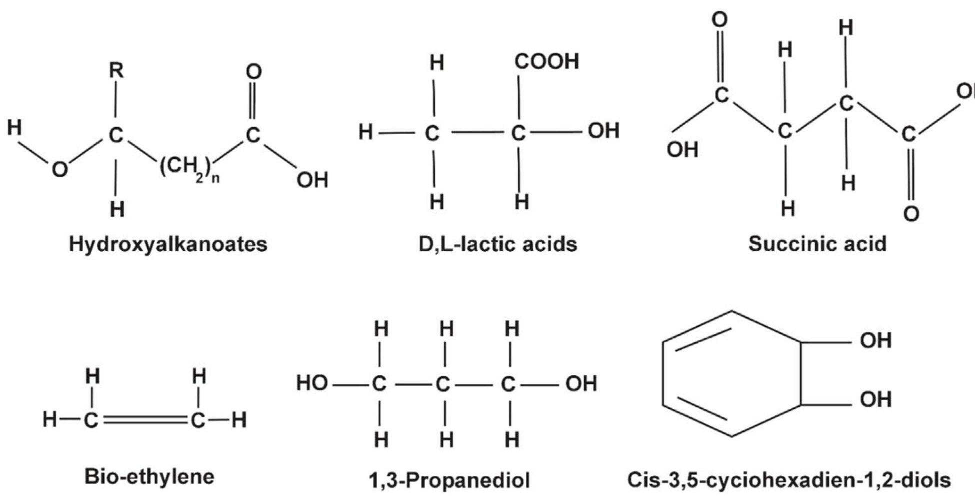

Fig. 1. The most common molecular building blocks of bio-polymers produced naturally by bacterial fermentation.

require any nutrient limitation (Muhammadi et al., 2015). For example, bacteria *Ralstonia eutropha*, *Pseudomonas oleovorans* and *Pseudomonas putida* belong to the first group, while, recombinant *Escherichia coli* belongs to the second one (Nitschke et al., 2011).

2.1. Structure of PHAs

About 150 different congeners of PHAs have been reported (Zhang et al., 2006). The general structure of PHAs is shown in Fig. 2. If the group is R = CH_3, the resultant polymer is called polyhydroxybutyrate or polyhydroxybutyric acid, while if R = C_3H_7, the polymer is called polyhydroxyoctanoate (PHO) and so on.

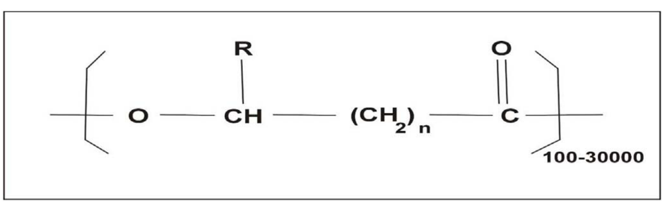

Fig. 2. General structure of polyhydroxyalkanoates with some modifications as reported in Ojumu and coworkers (Ojumu et al., 2004), Where if n = 1,R = methyl: poly (-3-hydroxybutyrate); R = hydrogen: poly (-3-hydroxypropionate); R = propyl: poly (-3-hydroxyhexanoate); R = nonyl: poly (-3-hydroxydodecanoate); R = ethyl: poly (-3-hydroxyvalerate); R = pentyl: poly (-3-hydroxyoctanoate); If n = 2, R = hydrogen: poly (-3-hydroxybutyrate); If n = 3, R = hydrogen: poly (-5-hydroxyvalerate).

2.2. Classification of PHAs

PHAs are classified into three classes of short, medium or long chain length (scl, mcl and lcl) respectively, according to the number of carbons in the side chains (Kunasundari and Sudesh, 2011). The scl-PHAs have less than 5 carbon atoms, while, mcl-PHAs have 5–14 carbon atoms and lcl-PHAs have more than 14 carbon atoms but are uncommon and less studied. The congeners of 3-hydroxyvalerate and 3-hydroxybutyrate are examples of scl-PHAs, while 3-hydroxydecanoate, 3-octanoate and 3-hydroxyhexanoate are of mcl-PHAs. Fig. 3 shows the general structure of PHAs with their classification. The mcl-PHAs were first observed in *P. oleovorans* in 1983 (Rai et al., 2011).

2.3. Properties of PHAs

Due to the structural variations in monomers constituting PHAs, they differ in properties and chemical composition as homo or co-polymers. PHB is comparable to polypropylene and shows good resistance to moisture and acquire excellent barrier properties to gases.

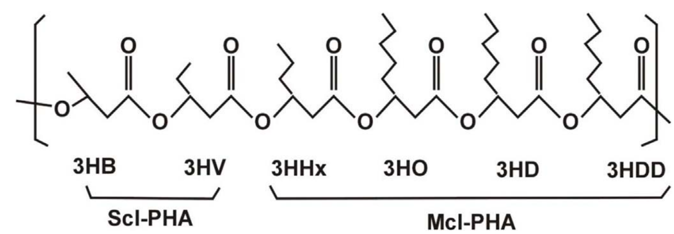

Fig. 3. Structure of PHAs with respect to classification, where 3HB = 3-hydroxybutyrate, 3HV = 3-hydroxyvalerate, 3HHx = 3-hydroxyhexanoate, 3HO = 3-hydroxyoctanoate, 3HD = 3-hydroxydecanoate and 3HDD = 3-hydroxydodecanoate.

PHAs are insoluble in water, have good resistance to hydrolytic attack, resistant to UV, sink in water which facilitates anaerobic biodegradation in sediments. In addition, they are biocompatible and biodegradable (e.g. undergoes degradation in soils) and behave as piezoelectric materials (Bugnicourt et al., 2014). PHAs also have chiral molecules and the degradation of PHAs depends mainly on their type and composition (Boyandin et al., 2013). Therefore, the biodegradation of PHAs is affected by the type and composition of the polymer, environmental conditions and the type of microorganisms (different microorganisms produce different PHA-depolymerases to degrade PHAs) (Masood et al., 2014).

PHAs are soluble in chloroform and other chlorinated solvents. Their glass transition temperature varies from −50 to 4 °C, melting temperature from 40 to 180 °C (Padermshoke et al., 2005). Thermo-degradation temperature, tensile strength, Young's modulus, water vapor and oxygen transmission rate vary according to the type of polymer produced and the composition of monomeric unit (Bugnicourt et al., 2014).

2.4. Microorganisms producing PHAs

Both prokaryotic and eukaryotic type of microorganisms can produce different types of PHAs. PHAs have also been reported in blood and tissues of human and animals (Rehm, 2009), and are used to control of seizure, metabolic disease and increasing cardiac efficiency. Different bacteria produce different type of PHAs. Fluorescent *Pseudomonas* strains, for example, are well known to accumulate mcl-PHAs as they have mcl-PHA synthases for the synthesis of PHAs with 6–14 carbon atoms (Kim et al., 2000).

2.5. Carbon sources on PHAs composition

The composition of the PHAs produced by different bacterial strain varies depending on the type of carbon source available. Such property