

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 8, Issue 3, March 2019

Polyesters, Carbohydrates and Protein based Bio-plastics, their Scope and Applications: A Review

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ABSTRACT: With the ever increasing demands of plastics in day to day lives, and its accompanying damages to the environment and ecosystems, it has become an inevitable quest to search for the alternatives for the petroleum based plastics. Biopolymers play an important role in the living systems and also many of them are being researched for these days to be utilized as an alternatives to synthetic plastic materials. This review paper focuses on the work done so far, in the fields of Bioplastics including Polyesters, Carbohydrates and Protein based plastics.

KEYWORDS: Bioplastics, PHB, Keratin, Biopolymers

I. INTRODUCTION

Plastic finds never ending uses in modern lives. It occupies a huge share in the market of domestic needs, packaging, storage and transportation. We have become so acclimate of using plastic in our daily routine that it seems almost impossible to imagine a world without plastic. Moreover, the bio-waste generated in the agriculture, poultry and other industries are also a challenge to be disposed off in a clean and hygienic manner especially in developing countries like India.

Though recycling of plastics have been taken up as a measure to reduce the environmental problems caused by it, it has so far achieved with minimum success and as a result most of the plastic waste end up in landfills [1]. The probability of bio- derived plastics being used as the alternate polymer of the petroleum based plastics is what sought to be a promising alternative.

So far, the bio-plastics from various sources of plants and animal origin are being studied and also few of them are available in market. The bio – derived plastics although also pose challenges, including the one with clashing needs of the food resources and also their incorporation into the plastic processing steps including extrusion, injection molding etc. To cope up with the challenge of conflicting interests with food resources, the focus is now shifting to generate bio – polymers from the waste generated in agricultural, poultry and other industries. This review, presents the current scenario of various types of bio – based plastics available in the market and also the potential biopolymers from the agricultural and industrial wastes that can be utilized to replace the petroleum based plastics in future.

II. RELATED WORK

The enormous detrimental impacts of petroleum based plastics have necessitated the search for the Bio materials that can serve as its alternative. Bio-polymers such as Polyoxoesters, Polylactic acid, Polysaccharides and Proteins are the substitutes of the petroleum based plastics currently being used and researched for [Fig.1] [2].

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Vol. 8, Issue 3, March 2019

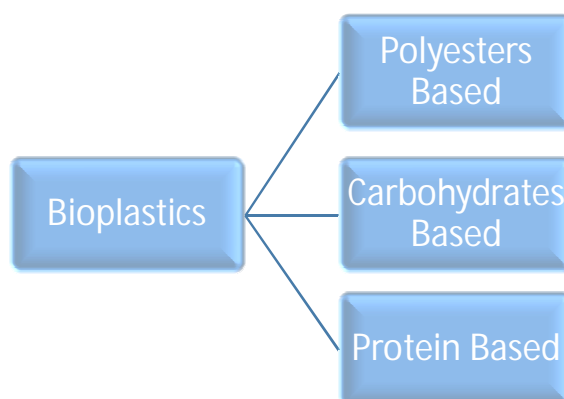


Figure 1: Types of Bioplastics

The polyesters like PHA and PHB are currently the most extensively studied biopolymers for their applications as bioplastics. These are the microbial polymers that have thermoplastic properties and could be isolated from a range of bacteria for various applications. Biopolymers including starch from number of sources have also being studied for their thermoplastic properties. Similarly the proteins like whey, soy, egg white, wheat gluten, and keratin have properties that could be exploited to yield polymers that can potentially replace petroleum based plastics and find various other biomedical applications.

III. POLYESTERS BASED PLASTICS

Polyhydroxy Alkanoate (PHA) and Polyhydroxy Butyrate (PHB) are the two microbial biopolymers that are mainly used as bioplastics. PHB was first identified in *Bascillus megaterium* by Lemoigne[3]. Polyhydroxyalkanoate(PHA) belongs to a group of polyoxoesters that have biodegradable thermoplastic properties[4]. PHA is produced by the bacteria grown under stress conditions or under limited essential nutrients concentrations like nitrogen, phosphorus or oxygen [5]. Many bacteria including arcaebacteira, Gram positive, Gram negative bacteria and Photosynthetic bacteria [6,7,8,9,10]are reported to produce PHA in unbalanced growth conditions. PHA is produced and accumulated by the microbes in the forms of granules[13]. The PHA granules are surrounded by phospholipid monolayer to prevent the PHA from coming in contact with water and getting converted into crystalline form [14].

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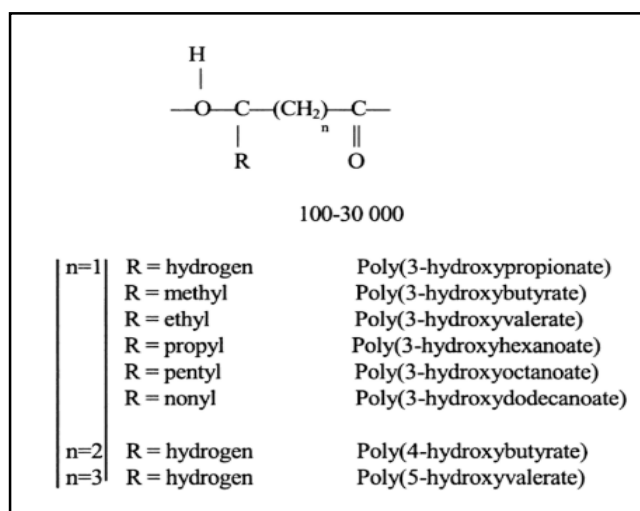


Figure 2: General Structure of polyhydroxyalkanoates (Lee,1996b)

PHA are structurally classified on the basis of their monomeric units and the number of carbon atoms which may vary from 4 to 14, Fig.2 [11, 12]. The R group could thus be a hydrogen atom, methyl group, ethyl group and so on. Different bacteria producing PHA under limited nutrient concentration are *C.necator*, *Protomonas extorquens* and *Protomonas oleovorans*[2]. Whereas those bacteria that can produce PHA in exponential growth phase are *Alcaligenes latus* and recombinant *E.coli* having operon responsible for PHA biosynthesis from *C. necator*[15,16]. Different bio-wastes including malt waste, baggase hydrolysate, Waste glycerol, waste frying oil, generated in Agricultural and Food processing industries have been studied to serve as the renewable and inexpensive carbon source.[17,18,19,20,21] Industrial bulk production of PHA have some major limitations including High cost of downstream processing and recovery as the bacteria producing PHA naturally are hard to lyse[22], difficulties faced as a result of slow growth due to unbalanced nutrient concentrations[23,24], and lastly challenges faced in utilizing waste materials as carbon sources.

The major drawback with the production of PHA based bioplastics is the production and recovery cost of fermentation and microbial culture procedures and thus these are not able to compete with the conventional petroleum based plastics. [25]

IV. CARBOHYDRATES BASED BIOPLASTICS

Complex polysaccharides like starch from various sources have been studied extensively for the production of bio-plastics. Starch can serve as the cost effective and also completely biodegradable source of bio based thermoplastics; hence many efforts have been made to develop products that can replace petrochemical alternates. The most common sources of food starch are potato, wheat, corn and rice [26]. Corn and potato starch based bio-plastics are already available in market and newer and innovative plant and animal material are being investigated as the replacements of the petroleum based plastics. Thermoplastic starch is made by processing starch and plasticizer mixture in an extruder high temperature, pressure and shear [27]. The addition of plasticizer like glycerol is important to obtain a rubbery material with minimum brittleness. [28].

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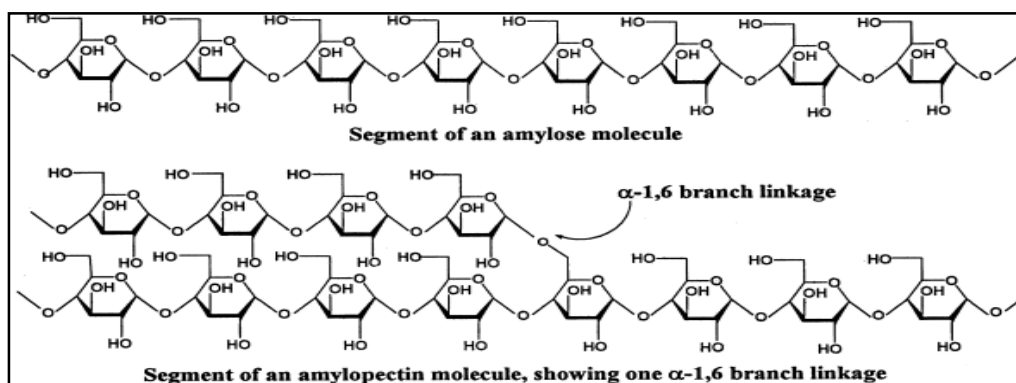


Figure 3: Basic Structure of Starch

Structurally starch is made up of two components- amylose and amylopectin, that contains α -1,4 glycosidic bonds along the straight chain and α -1,6 glycosidic bonds at the branch points [Fig3]. The degree of polymerization and number of α -1,6 linkages are higher in amylopectin than in amylose [40]. Cassava is also reported to be an important source of starch for the production of bioplastic [29]. Lucia Fama et al and others have reported the use of cassava starch for the manufacturing of biofilms. One important aspect of starch based bioplastic films is the amount of moisture content, as higher moisture content are associated with growth of microbes and texture alterations. Moisture content in cassava starch is reported to be 0.27%, which is supposedly lower than potato starch, maize starch and rice starch [30]. Improved water resistance have been reported by the combinations of starch with hemicelluloses, zein and polycaprolactone [31]. Citric acid when incorporated in glycerol plasticized thermoplastic starch showed improved thermal stability, decreased tensile strength and improved water resistance at high relative humidities [32]. Biodegradation of starch based plastic bags have shown in various ecosystems with weight loss of 37% and 43% in soil and compost upon incubation of three months [49,50].

The major drawback with the starch based bio-plastics is their abilities to uptake water. Higher water absorption properties make them unsuitable for the packaging of food products. Another problem associated with starch based bio-plastics is retro-gradation, in which the amylose and amylopectin chain undergoes realignment upon the cooling and ageing of the cooked starch. As a result of this retro-gradation, starch film tend to become crystalline and stiffer and loss of stretch ability. Fatty acids and lipid incorporation in the starch- glycerol films have been tested with limited improvements, and lipid incorporation is actually reported by Alberto Jiménez et al in 2013, to be associated with increased crystallinity [33].

V. PROTEIN BASED BIO – PLASTICS

Proteins are the most abundant in nature and also the most extensively studied biomolecules. They play variety of structural and dynamic roles in the living organisms ranging from sensitive immunoglobulins playing the central role in immune systems to the strength giving molecules like keratin present in the exoskeleton and the epidermal tissues and those performing structural and biological activities in plants [44, 45]. Along with biological functions, proteins are also used in various medicines, food and other industries.

Proteins owing to their secondary structures and wide range of bonds that can be formed between functional groups of individual amino acids, have now been explored to produce bio – based materials that can efficiently substitute the petroleum based plastics. Various proteins from animal and plant origin are being studied to make bio based plastics. Plant derived proteins include casein, Cocoa bean material, Corn gluten, Linseed meal, Sorghum meal, Soy, Wheat and Zein [34]. Those from animal origin are Abattoir waste and blood meal, Egg albumin, feather meal, fish protein, horn meal, leather scrap and microbial sludge [34].

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Vol. 8, Issue 3, March 2019

	Whey	Soy	Egg White	Wheat Gluten	Feather Keratin
Alanine	5.20	4.20	6.60	2.40	3.66
Cystine	2.20	1.30	2.50	2.10	2.11
Glycine	2.20	4.10	3.60	3.10	7.57
Isoleucine	6.00	4.80	6.00	4.00	4.93
Leucine	9.50	8.10	8.50	6.80	7.48
Methionine	1.90	1.30	3.60	1.80	0.03
Phenylalanine	2.30	5.20	6.00	4.90	4.11
Proline	6.60	5.10	3.80	13.70	1.01
Tryptophan	2.20	1.30	1.40	1.00	
Valine	6.00	5.00	7.00	4.10	7.24
Serine	5.40	5.20	7.30	5.20	13.57
Threonine	6.90	3.80	4.40	2.50	4.11
Tyrosine	2.70	3.80	2.70	3.80	1.85
Aspartic Acid	10.90	11.50	8.90	2.90	4.76
Glutamic Acid	16.80	19.00	13.50	37.30	9.18
Arginine	2.50	7.50	5.60	2.40	6.57
Hitidine	2.00	2.60	2.20	2.20	0.02
Lysine	8.80	6.20	6.20	1.20	0.57
Reference	34	34	34	34	38

Table 1: Amino Acid Composition of Proteins

The amino acid composition of various proteins used for producing bio based plastics is given in **Table1**. Egg White and wheat gluten based bio-plastics have been reported to behave like thermoplastics, their water absorption and retaining properties make them suitable to be used in active food packaging, absorbents and also in drug delivery systems [35]. Gluten has also been studied as blend with aliphatic polyesters to biodegradable plastics having good physical and thermal properties [41].

Mohanty et al have showed considerable improvements in the mechanical properties such as tensile properties, flexural properties as well as heat deflection temperatures of soy based bio-plastics by mixing with biodegradable hemp fiber [36]. Studies have shown that egg whites blends can be more easily processed than wheat gluten blends owing to their better rheological properties [42].

Another promising candidate suitable for the production of bio based plastics is keratin protein. Biofilms derived from keratin protein have been found to be suitable for wound dressing, tissue engineering scaffold, diffusion membrane, coating in implantable devices and cell encapsulation [37,46,47]. Arun Gupta et al and others explain the process to extract keratin protein from chicken feather [38,43]. Seongjae Shin et al states the use of microwave assisted extraction of human hair protein with extraction efficiency for 60 mins incubation similar to that of conventional methods taking 24hrs of incubation at 50 degree Celsius [48].

Navina Ramakrishnan et al have studied the use of keratin isolated from poultry waste feather for the production of bio – based plastics [39]. The Cysteine content of keratin in hair is 14 % that in feather is 7 % [34]. Amino acid cysteine is present in large amounts in the keratin protein [51]. Cystein (C) is a sulphur containing amino acid, the sulphur of which is involved in disulphide bonds (S-S) with other cysteine molecules. These disulphide linkages together with hydrogen bonds provide keratin its characteristic properties of stiffness and crystallinity [52]. The cystine bonds provide strength

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in solid state while it hinders with the processing of protein in liquid state [53]. For breaking these cystine bonds agents like Na_2SO_3 have been reported to be used in solution processing and thermal processing of these proteins [54].

The tensile properties of the bio based plastics derived from chicken feather keratin are reported to decrease with increasing glycerol (plasticizer) concentration, with the best mechanical and thermal properties at a concentration of 2% glycerol [34]. The tensile strength of keratin based bioplastic is reported to be lower than that of starch-based bioplastic [39].

Keratin based bio plastics belong to the second generation bio based plastics as the raw material being used is the waste material example the feather waste from poultry industry. As a result they do not conflict with the nutritional needs. The keratin based plastics are completely biodegradable and biocompatible [39] and therefore could replace the petroleum based plastics that are non- biodegradable and non – renewable.

VI. CONCLUSION AND FUTURE OUTLOOK

In the view of depleting petroleum resources, quest is on to manufacture plastics that are both biodegradable and comes from renewable source that do not have conflicting interests with the nutritional requirements of the people.

The plant based bioplastics shows promising properties but they can in future pose a threat to nutritional supply chain and may lead to uncontrolled deforestation for the massive production of bio based plastics. As far as the microbial bio based plastics are concerned, there thermoplastic properties have been shown to be comparable with that of petroleum based plastics but their downstream processing and purification steps are extremely cost intensive and thus cannot compete with existing petro based products.

Considering the protein based bio plastics, proteins from plant and other animal origin again pose the similar threats to nutritional supply as the carbohydrate based plastics. So, keratin is sought to be a promising candidate for the manufacturing of bio-based plastics. Researchers are now focused on keratin based bio-plastic from keratin wastes that can compete with existing but nearly depleting petro- based plastics. [1, 30]

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