



Reviews on Biosynthetic Sustainable Polymers

S.Sharma^{a*}, S. Mounika^b, K. Sowmiya^b

- a. School of Textile Engineering, Kombolcha Institute of Technology, Wollo University, Ethiopia.
- b. Department of Textile Technology, Bannari Amman Institute of Technology, Tamilnadu, India.

How to cite this paper:
https://xxxxx*

©2022 Kombolcha Institute of
Technology, Wollo University



ISSN : 2788-6239 (Print)
ISSN: 2788-6247 (online)

*Corresponding
Author:
drsandeep9751@gmail.com

ABSTRACT

Textile and clothing sectors are now in pressing need of sustainable materials to thwart the un-sustainability, which has originated from large scale disposal of certain contemporary fiber based products. Biosynthetic degradable polymers obtained from renewable materials have emerged to cater the demand for sustainable textiles. Biological products, such as starch and cellulose based polymers, have been in use for more than thousands of years as food, home furnishings and for Apparel. However, with improved understanding of science, technology and processing of biological products have experienced resurgence, with substantial industrial production. Continuous development in the production technology had enhanced the properties of natural polymers, such as heat resistant polylactic acid, enabling a wider range of applications. The sustainable disposal of synthetic fibres has been considered to be the principal driving force in stimulating the growth of biodegradable synthetic fibres. Polyhydroxyalkanoates, Poly-butayrate, Poly-caprolactone, Polylactic acid, Polytrimethylene terephthalate, Soyabean protein fibre, Casein and Chitin and Chitosan are some of the recently developed biopolymers promoting the sustainability. These biopolymers are becoming increasingly accepted for their attractive properties and their potential diverse applications. This article presents a critical review on existing natural renewable resources for the production of sustainable biosynthetic materials for textile application.

Keywords: Biosynthetic, Biodegradable Polymer, Sustainable Polymer, Polylactic Acid, Polytrimethylene Terephthalate.

1. INTRODUCTION

In the 21st century the term “sustainability,” a catchphrase inseparable from manufactured products, is being widely acknowledged by economists, environmentalist (environmentalists) and legislators. Most of the synthetic polymer based fibers, the primary re-

source for most textiles and apparel production having been synthesized from the crude petroleum, have registered tremendous growth since the 1950s. It is clearly evidenced by the Paris world environment safety summit that these synthetic polymers have largely contributed to environmental pollution. Large quanti-

ties of non-biodegradable plastic waste, consisting of turn-down sacks, carrier bags and wrapping, are being buried in landfill across the world every year. The disposal routes such as recycling and incineration are possible for these materials, but mix-up of various materials is posing problems to the domestic and industrial waste streams and separation is costly particularly for small items. Increased greenhouse emissions leading to global warming is an added problem. Nowadays, the biodegradable and biosynthetic polymers synthesized from natural annually renewable crops, are emerging as a source of raw materials for various applications including textile and clothing.

A sustainable biosynthetic and biodegradable textile product is defined as a material designed, produced, transported, used and discarded with due thoughtfulness by taking into account the environmental, social and economic implications. Nevertheless, with the application of biotechnology in polymer engineering, numerous efforts have been made to improve the biodegradability of existing PET. This is achieved by substituting weak link co-monomer such as ether, amide or aliphatic monomers in the molecular chain which promotes the biodegradation through hydrolysis. Biosynthetic polymers are engineered to degrade when disposed of in nature by the action of living or non-living microorganisms converting them into biomass. However, the synthesis and continuous production of these biosynthetic sustainable polymers from the annually renewable resources is one of the toughest challenges for the polymer industry. In the past decade an unexpected growth has been seen in the improvement of technology, processes and products derived from naturally renewable polymer resources such as; starch, cellulose and lactic acid. Poly-lactide or Poly (lactic acid) PLA, Polytrimethylene terephthalate (PTT) and Polyamide 11 (PA11), Soyabean protein fibre (SPF), Milk (Casein) and seafood (Chitin and Chitosan); the emerging biopolymers are being increasingly accepted due to their eco-friendly properties

and potential for diversified applications with negligible or no ecological impact. Renewable biopolymers have a significant contribution towards the development of a wider range of disposal materials with negligible impact on the environment. The market potential for these environmentally friendly, biodegradable polymers are growing at a rate of 10–20 % annually [2]. For Biosynthetic polymers, the main constituents of production are obtained from renewable resources and are also synthesized from fossil resources [3]. The prospect of biodegradable polymers has been acknowledged for a long time as an ultimate resource to overcome the drawback of petrochemical resources. However, biodegradable polymers have not found extensive applications in industries to principally replace synthetic crude petroleum based plastic materials; reasons being high production costs and under-performing properties. This overview on biosynthetic and sustainable polymers briefly goes over the progress, technical, social challenges and ecological merits of biodegradable polymers and covers all natural polymers which are either in developing stage and or already at marketed stage.

2. HISTORY OF BIOSYNETHETIC DEGRADABLE POLIMER

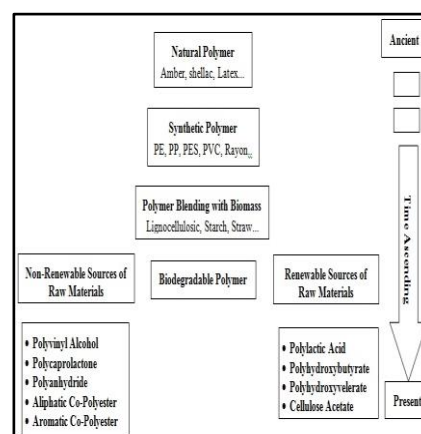


Fig.1 Trend in biopolymer development [4]

Human race is using biodegradable polymer since time immemorial. The best known example is the natural gum derived from plants used to join two wooden pieces and later to provide hydrophobic properties to

the boat making materials. Natural rubber a biodegradable polymer is known to the mankind since 1495. Figure 1 illustrates the stages of development in biodegradable polymer starting from natural polymer.

2.1 Biosynthetic Degradable Polymers

Biosynthetic polymers are those synthesized from biodegradable annually renewable resources. These are also sometimes referred to as agro polymers such as starch, chitin, protein, biodegradable polyesters such as poly-hydroxyalkanoates, polylactic acid, and polypeptides etc. The concept of renewable biosynthetic polymer cannot be explained without understanding the complete carbon cycle. The carbon cycle is a complex process by which carbon is exchanged between the four main reservoirs of carbon on the planet i.e., the lithosphere (e.g., limestone), the biosphere (plant and animal), the hydrosphere (e.g. bicarbonate dissolved in the oceans), and the atmosphere (CO₂). According to the definition of ASTM D-5488-94d and European norm EN-13432, biodegradable resource is defined as capable of being breaking down into carbon dioxide, methane, water, inorganic compounds, and biomass under the action of microorganisms [3],[5]. Degradation of a degradable polymer is measured in terms of duration of application or in relation to human lifetime rather than on absolute time frame. A distinction between degradable and non-degradable polymer can be made by defining a Deborah number which is dimensionless (D). Deborah number is defined by the equation 2.1

$$D = \frac{\text{Time of degradation}}{\text{Human life time}} \text{-----} 2.1$$

For biodegradable polymers $D = (D \rightarrow 0)$ and for non-biodegradable polymers $D = (D \rightarrow \infty)$. The biodegradability of the resource can be assessed by subjecting the material to different media such as liquid, inert, or compost medium [6]. The Figure2 succinctly illustrates the process of natural recycling of the biodegradable polymer originated from natural renewable resource.

The mechanism is the enzymatic action of microorganisms can be measured by conducting standard tests over a specific period of time. Biodegradation of polymeric materials is looked upon from the chemical perspective.

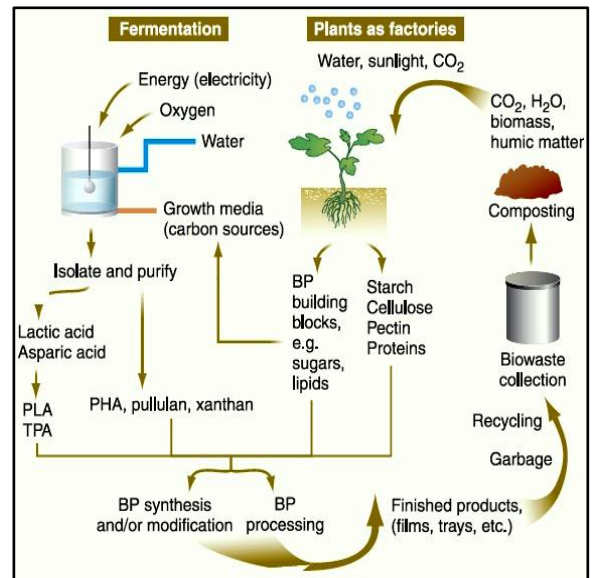
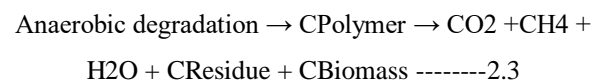
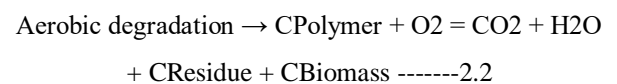


Fig. 2 Process of natural recycling biodegradable polymers [7]

The key degradation process is represented by equations 2.2 & 2.3 as shown below.



2.2 Mechanisms of Polymer Degradation

Polymer biodegradation is known as degradation caused by biological and non-biological activity. Different mechanisms of hydrolysis are usually present in most environments. In enzymatic degradation material is degraded gradually from the surface of the substrate to inwards and in contrast, chemical hydrolysis of a solid material can take place throughout its cross-section, except for very hydrophobic polymers. Biological degradation takes place through the actions of enzymes or by products (such as acids and peroxides) secreted by microorganisms (bacteria, yeasts, fungi). Also, microorganisms can eat, and sometimes digest polymers, and cause mechanical, chemical and

enzymatic ageing. Two steps occur in the microbial polymer degradation process, first, a de-polymerization or chain cleavage step, and second, mineralization. De-polymerization normally occurs outside the organism due to the size of the polymer chain and the insoluble nature of many polymers. Extracellular enzymes are responsible for either endothermic or exothermic process which initiates the biodegradation. During the degradation process the cell usually derives metabolic energy from the mineralization process and release by products such as gases, water, salts, minerals and biomass. Biodegradation process can occur, depending on the polymer, the organisms and the environment. At a particular stage in the degradation process, involvement of enzymes is unavoidable. Enzymes are either living or non-living biological catalysts that can induce substantial increases in reaction rates in an environment that is otherwise un-favourable for chemical reactions. The enzyme activity is closely related to the conformational structure, which creates certain regions at the surface forming an active site. At the active site the interaction between enzyme and substrate takes place, leading to the chemical reaction, eventually giving a particular product. For optimal activity most enzymes must associate with cofactors, which can be of inorganic or organic origin.

2.3 Classification of Biodegradable Polymers

Biodegradable polymers are categorized into three main categories [8-10] :

- 1) Natural polysaccharides and biopolymers (e.g. cellulose, alginates, wool, silk, chitin, soya bean protein)
- 2) From Biotechnology, Synthetic polymers, particularly aliphatic polyesters [e.g. poly (lactic acid), Poly (ε-caprolactone).
- 3) Polyesters produced by microorganisms (e.g. polyhydroxyalkanoates)

Figure 3, illustrates the basic division that becomes the starting raw material for the production of biodegradable polymers.

The agro based biodegradable polymers are divided into two main categories namely: Polysaccharides and Proteins.

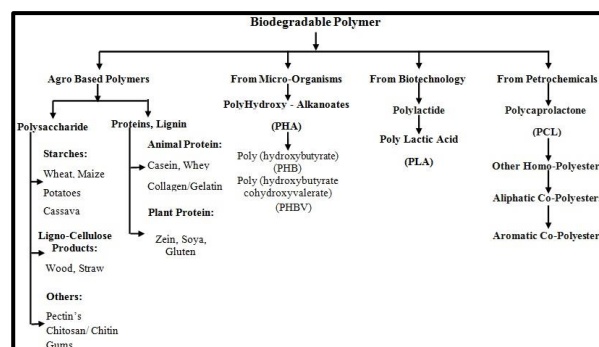


Fig 3: Basic root of the biodegradable polymers [8]

2.3.1 Polysaccharides

Polysaccharides are the most abundantly available macromolecules in the biosphere. These complex carbohydrates constituted of glycosidic bonds are often one of the main structural elements of plants and animals exo-skeleton (cellulose, carrageen and chitin).

Polysaccharides can be further divided into three types namely Starches, Ligno-cellulose and Petin's/Chitosan/Chitin/gums.

2.3.2 Starches

Starch is a well-known low cost polysaccharide abundantly available hydrocolloid biopolymer [11]. Starch is produced by plants in the form of granules, which are hydrophilic. The common sources of starch include potatoes, corn, wheat and rice. It is composed of amylose (poly- α -1,4-D-glucopyranoside), a linear and crystalline polymer and amylopectin (poly- α -1,4-D glucopyranoside and α -1,6-D-glucopyranoside), a branched chain amorphous polymer. Depending on the resource starch is composed of different proportions of amylose and amylopectin ranging from about 10–20% amylose and 80–90% amylopectin [12]-[14]. Figure 4 illustrates the amylose chains, a single or double helical conformation with a rotation on the (1→4) linkage [15]. The amylopectin has the same monomeric unit as amylose as indicated in Figure 5.

Thermoplastic starch or plasticized starch offers an attractive alternative for synthetic polymers in specific applications such as natural fiber reinforced composites.

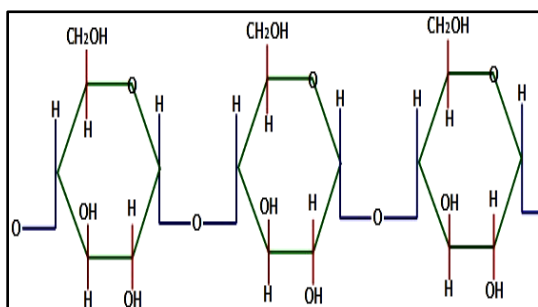


Fig. 4 Structure of amylose molecule

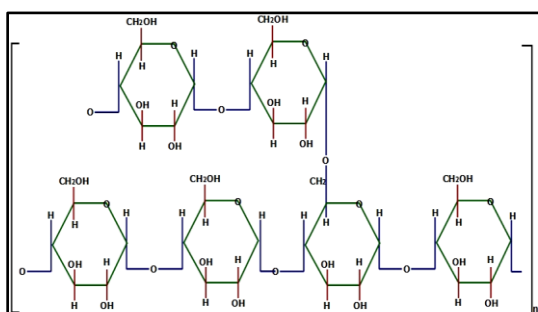


Fig. 5 Structure of amylopectin molecule

In the recent years considerable research has been focused on developing a new class of biodegradable or green composites referred as bio-composites consists of a biodegradable polymer combined with natural fibres as reinforcements [16].

2.3.3 Cellulose and Cellulose Acetates

Cellulose is another widely known polysaccharide produced by plants composed of long linear macromolecular chains of one repeating unit, known as cellobiose usually crystalline, infusible and insoluble in all organic solvents [17]. Biodegradation of cellulose proceeds by enzymatic oxidation, with peroxides secreted by fungi. Figure 6 shows the molecular structure of cellulose. Because of its insolubility and infusibility, cellulose should be transformed to be process-able. Ethers, esters and acetyls, the derivatives of cellulose are produced by reaction of one or more of the hydroxyl groups present in the repeating unit. Tenite®,

Bioceta®, Fasal® and Nature-flex®; are some of the well known trade names of cellulose based polymers. Cellulose esters are modified polysaccharides. Large degree of substitutions can be made; however, the mechanical properties are inversely proportional to the degree of substitution.

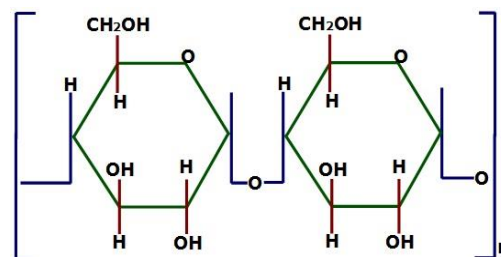


Fig. 6 Molecular structure of cellulose

Cellulose acetate (CA) is one of the most important cellulose derivatives. Research studies carried out in computer-generated compost environments revealed that cellulose acetates with degrees of substitution up to 2.5 are said to be biodegradable [18]. A decrease in the degree of substitution of cellulose acetate from 2.5 to 1.7 results in a large increase in the rate of their biodegradation. A fully biodegradable cellulose acetate has been developed by "Eastman Chemical" [19], [20].

2.3.4 Chitin and Chitosan

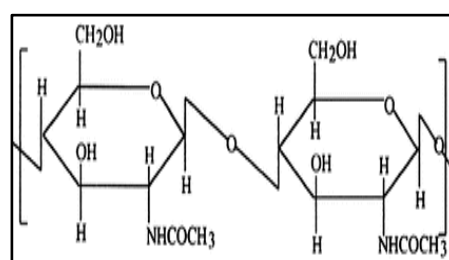


Fig. 7 Chemical structure of chitin

Chitin is the second most important biopolymer largely found in marine objects such as shells of crabs, shrimp, crawfish and insects.

It is a linear copolymer of N-acetyl glucosamine and N-glucosamine with beta-1,4 linkages randomly or block distributed throughout the biopolymer chain depending

on the processing method used to obtain the biopolymer as indicated in Figure 7.

Development in fermentation techniques suggest that the cultivation of fungi can provide an alternative source of chitin [21]. Chitin is processed to chitosan by partial alkaline N-de-acetylation in which glucosamine units are predominant. The ratio of glucosamine to acetyl glucosamine is reported as the degree of deacetylation ranging from 30% to 100% depending on the preparation method; however, it affects the crystallinity, surface energy and degradation rate of chitosan [22]. Chitosan is insoluble in water and alkaline media due to its rigid and compact crystalline structure and strong intra- and intermolecular hydrogen bonding. Figure 8 shows the molecular structure of Chitosan.

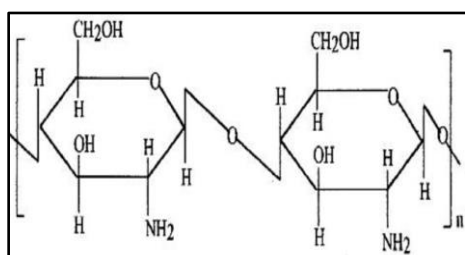


Fig. 8 Chemical structure of chitosan

Chitosan is soluble only in a few dilute acid solutions hence, for spinning of biodegradable films it is essentially dissolved in acidic solutions [23]. Enzymes such as chitosanase or lysozymes are known to degrade chitosan. Customized chitosan have been prepared as N-carboxymethylchitosan or N-carboxyethylchitosan for its use in cosmetics and in wound treatment [24]. Chemical modifications of both polymers are of special interest, due to their retention of polymer basic molecular structure and their physical and biochemical properties; thus, numerous derivatives have been developed in the past decade [25]-[27].

2.3.5 Proteins

The term “protein” comes from the Greek, proteios, for “primary, first and foremost”. Proteins are thermoplastic hetero-polymers. They are constituted by both polar and non-polar α -amino acids. Amino acids

are able to form a lot of intermolecular linkages resulting in different interactions as indicated in Figure 9. These offer a wide possibility of chemical functionalities and functional properties [28].

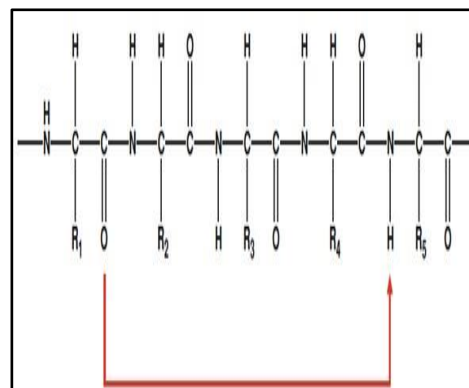


Fig. 9 Chemical structures of primary protein and interaction between the amino acids indicated by red arrow

In terms of potential resources, soya protein, corn protein and wheat proteins are among the main plant proteins however, the Casein, collagen protein or gelatine, and keratin proteins obtained from animals. The bacterial proteins include; Lactate dehydrogenase, chymotrypsin, and fumarase etc. The majority of the proteins are neither soluble nor fusible, especially fibrous proteins as silk, wool and collagen [29]. A definite number of protein have received much attention by the research community as biodegradable polymers but a few have led to actual industrial scale-up due to their high cost of production and low product performance. Generally, proteins consist of linear polymers chains built from a series of up to 20 different amino acids and are folded into 3D structure [30]. The process-ability, flexibility, and extensibility of proteins films are improved by mixing them with plasticizers [31], [32]. Proteins usually biodegrade naturally in the presence of enzymes, as protease, and is an amine hydrolysis reaction and the biodegradation rate can be controlled by grafting [17].

2.3.6 Collagen

Collagen is a primary protein mainly extracted from animal's tissues. There are in total thirty different types

of collagen protein that have been identified in nature. Collagen is a complex biological molecule consisting of different polypeptide,

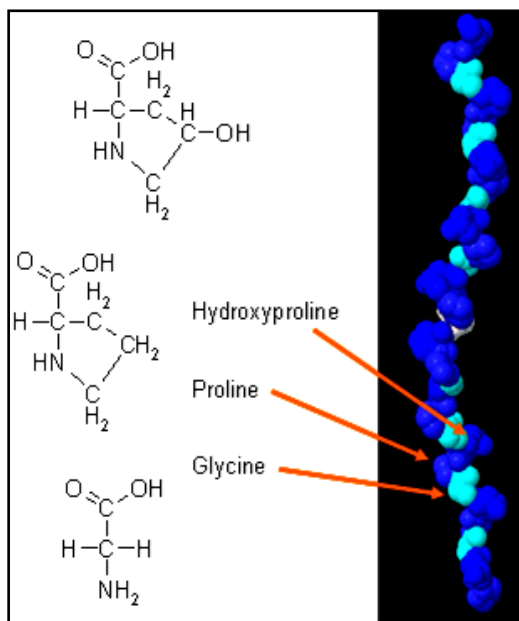


Fig.10 Molecular structure of Collagen and its main constituents

mainly the glycine, proline, hydroxyproline and lysine as building blocks as indicated in Figure 10.

Glycine is the main component of collagen molecular chain which makes it elastic; however, the elastic behaviour of the molecular chain can be manipulated by regulating the amount of glycine [33]. The Collagen is enzymatically degradable and possesses unique biological properties and has been extensively studied looking in at its potential application in the field [34]. The biodegradation of proteins is achieved by enzymes, as protease, and is an amine hydrolysis reaction.

De-polymerisation or degradation of collagen results in a high molecular weight polypeptide termed as gelatin, a kind of protein that consists of 19 amino acids [78]. The molecular structure of gelatin is shown in Figure 11.

It is usually water soluble and possesses good film forming properties. The mechanical and physical properties of these films depend on the properties and characteristics of the gelatine, especially the amino

acid composition and the molecular weight distribution.

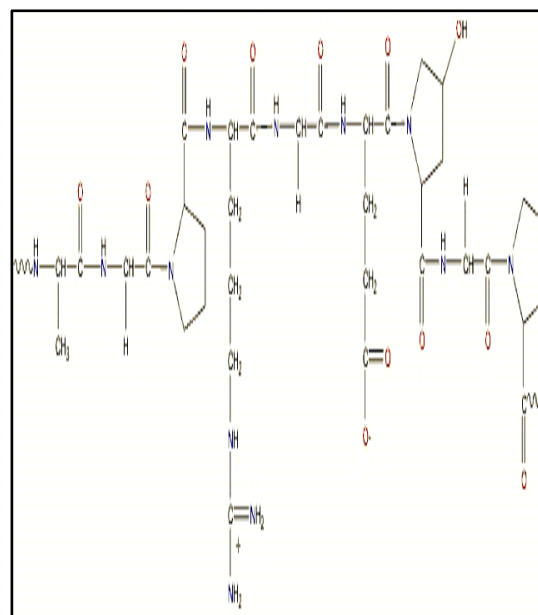


Fig. 11 Molecular structure of Gelatin

2.3.7 Micro-organisms Based Degradable Polymers

Polyesters are obtained by polymerisation of natural monomer units prepared by fermentation process or produced by a range of microorganisms, cultured under a diverse range of renewable resources and ecological settings [35]. Fermentation of naturally occurring sugars produces different monomers which are transformed into polymers [36],[37]. In the early 1970's it was already known that poly(ϵ -caprolactone) degrades when disposed to bioactive environments such as soil [38]-[40]. Crude petroleum based synthetic polyester are hydrophobic in nature and usually melt-spun into a wide variety of products such as sheets, bottles and shaped articles which are resulting into landfills ~~are~~ targeted for replacement by biodegradable polymers. There are many types of biodegradable polyester available in the market and some of them are in of developing stage. The most important biodegradable are Polyhydroxy-alkanoates, Polylactic-acid (PLA) Polybutylene-succinate (PBS), Polycaprolactone (PCL), Polytrimethylene (PTT) and Polyamide-11 (PA-11), are briefly discussed.

2.3.8 Polyhydroxy-alkanoates (PHA) Polyester

Polyhydroxyalkanoates are inevitably a key biopolymer belonging to the family of intracellular biopolymers from renewable resources i.e. microbes [41-44]. PHAs can also be produced by plants or transgenic plants [45, 46]. A number of bacteria can accumulate PHAs as intracellular reserve materials. Some organisms accumulate PHA from 30% to 80% of their cellular dry weight, in the presence of an abundant source of carbon and under limited nitrogen [47]. The main biopolymer of the PHA family is the polyhydroxybutyrate homo polymer (PHB). In recent years, there has been growing interest in the use of PHB and PHB co-polymers in the biodegradable plastics industry. The eco-friendly and non-toxic effect of PHBs makes them a strong possibility for many medical applications, including drug release, bone regeneration, and nerve guidance etc; [48]. There are other polyhydroxybutyrate-cohydroxyalkanoates copolyesters exist such as polyhydroxybutyrate-co-hydroxyvalerate, polyhydroxybutyrate-co-hydroxyhexanoate (PHBHx), polyhydroxybutyrate-co-hydroxyoctanoate (PHBO), and polyhydroxybutyrate-co-hydroxyoctadecanoate (PHBOd). Figure 12 shows the generic formula for the PHAs where $x \geq 1$ or higher, and R can be either hydrogen or hydrocarbon chains of up to around C16 in length.

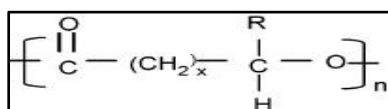


Fig.12 Generic chemical structure of Polyhydroxyalkanoates

ICI Zeneca commercialized PHAs produced by microbial fermentation in the late 1980s, under the trade name Biopol. Initially Biopol was used the polymer to make shampoo bottles. The physical properties and environmental acceptability of PHAs can be regulated by blending them with synthetic or natural polymers. The PHAs extensively synthesize by microbes matched by a corresponding abundance of microbes

that produce PHA-degrading enzymes and have plastic-like properties; however, their ecological acceptance makes them an attractive material to replace non-degradable polyethylene and polypropylene. The major drawback for broad applications of these polymers is their high production cost [49].

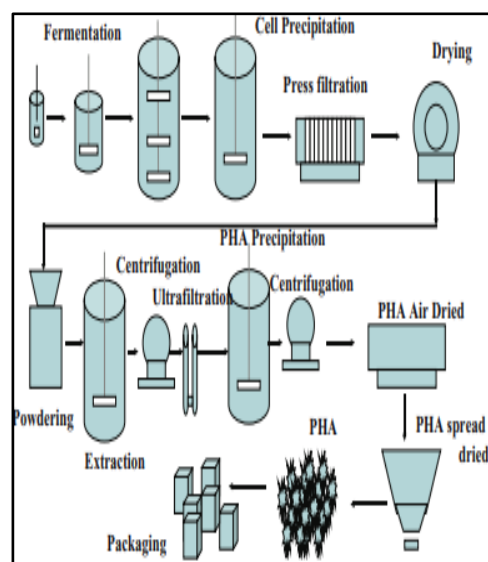


Fig. 13 General production and extraction process of PHA

However, numerous efforts have been made to reduce the production cost by exploring new cheap raw materials [50], [51]. Recent research indicates that the copolymer in *Escherichia coli*, has significant potential to reduce production cost and simplify refining process. Boston-based Meta-bolix has been well-known for established commercial production of PHA. Figure 13 illustrates the schematic of the production and extraction process followed, which has received many awards from various organizations for its environmental protection efforts [77].

2.3.9 Polylactic Acid (PLA)

PLA is a linear chain of recyclable thermoplastic aliphatic polyester derived from renewable agriculture resources such as; corn, sugarcane and beetroot etc [52]. The discovery of PLA dates back to the 1920s by Wallace Carothers. Polylactic acid is derived from a monomer of lactic acid and technically defined by, Federal Trade Commission [53]. PLA fibres are con-

sidered as a totally novel class of synthetic fibres produced from renewable crops and are melt-spinnable [54]-[57]. Early versions of fibers derived from PLA suffered from low temperature melting points. However, more heat resistant variants have been developed. Biofront, a polymer based on PLA is intended for use in clothing applications. Its high melting point of 210°C is better than conventional PLA fibers, which melt at 170°C. Teijin currently operate a pilot plant with an annual production capacity of 200 tonnes, and recently acquired Toyota's demonstration plant with 1000 tonnes capacity. Nature Work's LLC, another producer of PLA, with a trade name of Ingeo have an annual production capacity of 140,000 tonnes [58]. There are three basic production routes i.e.; Direct condensation polymerization forms low molecular weight PLA. Theophile Jules Pelouze was the first person to synthesize Polylactic acid by poly-condensation of lactic acid in 1845 [59]. Two steps polymerization i.e. Ring opening polymerisation (ROP), which results in higher molecular weight, but is still limited by the equilibrium reaction of poly-condensation due to hydrolysis of ester bonds [60].

Azeotropic Polycondensation and Solid state polymerization are two main and efficient synthesis methods identified in the recent years. An Azeotropic distillation using a high boiling solvent to derive the removal of water in the direct esterification process to obtain high molecular weight PLA was patented by Mitsui Toatsu Chemicals. Nature Works LLC, has developed a cost effective continuous process for production of lactic acid based polymers combining the substantial ecological and economic benefits of synthesizing both lactide and PLA in the melt rather than in solution and provides a commercially viable compostable commodity polymer [61], as indicated in Figure 14 below. The properties of PLA, as a textile fiber, resemble to commonly available thermoplastic fibres, in terms of crimp, surface characteristics, and low hydrophilicity.

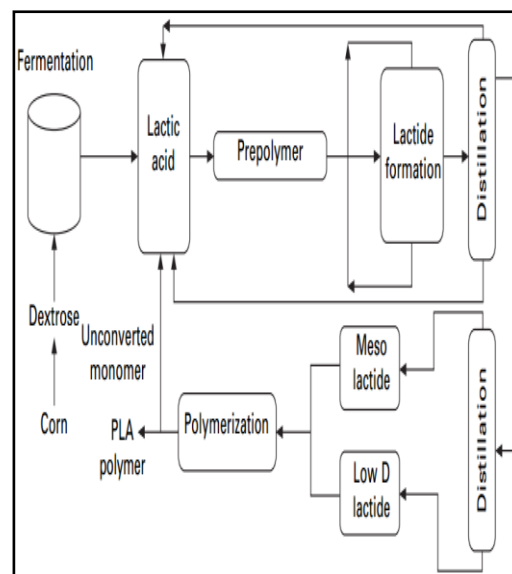


Fig. 14 Non-solvent process for PLA production (Nature works LLC)

Fabrics produced from PLA provide a silky feel, durability, and moisture-management properties and are expected to provide an alternative to materials derived from petroleum on both cost and performance basis including its functional and technical aspects. It has the potential to provide the textile industry with a novel product option, viz. an eco-friendly synthetic polymer, which can be used in a range of apparel and non-apparel fabric applications [62]-[65]. Many of its properties are comparable to those of polyethylene terephthalate (PET) fibre for example, its dimensional stability and crease resistance [62], [64], [65]. However, because it possesses superior moisture management properties, fabrics containing PLA are being considered for use in medical, sportswear or active wear, technical textiles, nonwovens, apparel fashion and home furnishings and other outerwear outfits.

2.3.10 Polycaprolactone (PCL) and Polyakylene – Succinates (PAS)

PCL is thermoplastic biodegradable polyester synthesized by chemical conversion of crude oil, followed by ring-opening polymerization resulting in to a partially crystalline material having a T_m of 59-64 °C and a T_g of -60 °C [48], [66]. The polymer is regarded as tissue compatible and was originally used in the medical field

as a biodegradable suture. Because the homo-polymer has a degradation time of the order of two years, co-polymers have been synthesized to accelerate the rate of bio-absorption. The most important properties of PCL include excellent water, oil, solvent, and chlorine resistance, a low melting point, low viscosity, and is easily process-able thermally hence can be used for variety of applications. Blending of PCL with fiber forming polymers such as cellulose, has facilitated the production of hydro-entangled nonwovens, scrub-suits, incontinence products, and bandage holders[67]. The molecular weight and degree of crystallinity decides the hydrolysis rate and biodegradation of PCL. PCL is predominantly used as a component in polyester/starch blends such as Mater-Bi as produced by Novamont. Caprolactone limits moisture sensitivity, boosts melt strength, and helps plasticize the starch. In contrast to PCL, PLA from lactide, and PHAs, a series of biosynthetic polyesters have been primarily developed by using the traditional polycondensation techniques[7].

2.3.11 Polyglycolide (PGA)

Polyglycolide (PGA), biosynthetic aliphatic polyester highly crystalline was first 100% absorbable suture, marketed as Dexon in the 1960s by Davis and GeckInc., originally located in Brooklyn, NY. Glycolide monomer is synthesized from the de-polymerisation of glycolic acid however Ring-opening polymerisation yields high molecular-weight materials, with approximately 1-3% residual monomer present. Due its high degree of crystallisation 45-55%, high melting point (220-225 °C) and a glass transition temperature of 35-40 °C, makes it not soluble in most organic solvents; the exceptions are highly fluorinated organics such as hexa-fluoro-isopropanol. PGA fibers exhibit high strength and modulus and are too stiff to be used as sutures except in the form of braided material however, accompanied with several advantages such as loss of about 50% of their strength after two weeks and 100% at four weeks, and are completely absorbed in 4 to 6

months. Polyglycolide polymer has been co-polymerised with other monomers to reduce the stiffness of the resulting fibers. Polytrimethylene terephthalate was first synthesized and patented in 1941. However until 1949 it was not produced commercially due to one of its the expensive precursor, 1,3-propanediol (PDO) in 1960's and ethylene oxide hydro-formulation was developed as an alternative [68]. In the early 1990s, hydro-formulation catalysts were created to allow for the economic formulation of PDO through continuous EO hydro-formulation [68, 69]. It has recently received much attention as an emerging fibre under the brand name "Sorona" by DuPont. PTT is synthesized from the condensation polymerisation of petrochemical-derived terephthalic acid and 1,3-propanediol, which in the case of Sorona is derived from sugar. Sorona fibres are claimed to possess good stain resistant properties, have a soft handle, with high strength and stiffness characteristics [70]. PTT is commercially produced by Shell Chemicals and marketed under the trade name "Corterra" has many characteristics that makes it suitable for a variety of applications due to superior elastic recovery, good colour fastness, uniform dye uptake, stain resistance and low static-charge generation. These developments may allow PTT to effectively compete against PBT and PET, two polyesters that have been far more successful than PTT to date. PTT is dye-able without a carrier at boiling temperatures under atmospheric conditions due to its open molecular structure, providing colour fastness comparable to nylon with select dyes [71]. PTT allows for additional tonal shades with pressure dyeing giving designers more choices for textile colours [72]. Dispersed dyes work best on PTT fibers, yielding a uniform colour with good fastness [69], [73].

3. CONCLUSION

This paper presents a critical review on various recently developed biosynthetic fibers and their poten-

tial. Development of sustainable biosynthetic polymers has been considered in the wider perspective of the green industrial revolution to reduce emission of the greenhouse gases to the environment due to its volume [74]. Recent developments in the genetic engineering of metabolic pathways have significantly enhanced the conversion of renewable feed-stocks to biodegradable polymer building blocks such as lactic acid [75]. Cloning and expression of genes in plants open up several possibilities for using photosynthesis to directly synthesize polymers in plants and can lead to cost-effective biological routes to produce monomers and polymers however, a broad range of synthetic biodegradable resins based on aliphatic and aromatic co-polyesters have been commercialized globally [76]. In contrast to, contemporary polymers, bio derived polyesters break down rapidly in to CO₂ and water in appropriate conditions where they are exposed to the combined attack of water and microbes and meet composting standards laid down by US, European, and Japanese, typically breaking down in twelve weeks under aerobic conditions. The PHA-based biodegradable polymers market is still very much at the developmental stage with few commercial applications. In 2005, market tonnage was estimated at no more than around 250-300 tonnes worldwide [48]. Assuming that producers are successful in bringing down PHA production costs and prices, and in developing niche applications, market tonnage could be around 4,500 tonnes by 2020. PBA Nodax has superior biocompatibility compared to other bio-resorbable polymers, which makes the material suitable for some medical applications such as drug release, bone regeneration, and nerve guidance. Nodax can be blended with other biodegradable polymers such as polylactic acid and thermoplastic starch for improved processing performance. Biosynthetic polyesters like polycaprolactone or polybutyleneadipate are eco-friendly, but their melting points of 60°C, are not suitable for many textile applications. Polycaprolactone market valuation is

anticipated to increase at a CAGR of 10% over the forecast period of 2021 to 2031 and reach a valuation of US\$ 545Mn by 2031 [78]. Polylactic acid is polyester made from the polymerisation of lactic acid; renewable resources such as corn starch and sugarcane are fermented by bacteria to produce the lactic acid. The PLA polymer is processed into fibre using conventional melt spinning processes. Polylactic acid is still in development as a textile fibre, particularly more heat-resistant variants.

Polylactic based fibres exhibit improved water absorbance and moisture transmittance properties, in comparison to polypropylene, nylon, and polyester, allowing for improved breathability of garments such as shirts, dresses and underwear. Further work is required to demonstrate the viability of using PLA fibres in textile applications due to initial problems with low melting temperature of current materials. PLA is the most widely used biodegradable polymer in the Asia Pacific region accounting for nearly 40% of total consumption as in 2005 and estimated to grow by the volume approx. 3.6 billion kg/year. The global PLA market size was USD 698,200.9 thousand in 2020 and is projected to reach USD 2,306,708.2 thousand by 2028, exhibiting a CAGR of 16.3% during the forecast period [79]. If these polymers displace an equivalent amount of fossil fuel based contemporary fibres, then 192 trillion of fossil derived fuel will be saved per year, resulting in a reduction in the emission of CO₂ by 10 million tons [48, 66]. Polytrimethylene terephthalate is a synthetic fibre produced from a partially renewable feedstock having similar properties to polyester but not fully biodegradable. Sugar cane is the main starting material for production of dextrose, which is then fermented and purified to produce 1,3 propanediol and is then melted with purified terephthalic acid (PTA) as in polyester production to form PTT. DuPont's "Sorona" fibres are claimed to possess good stain resistant properties, have a soft handle, with high strength and stiffness characteristics. Synthetic

biodegradable polymers are expected to show the fastest growth rate in the coming years due to extensive focus on environment friendly materials.

REFERENCES

- [1] A.Bergeret,A, “Environmental - Friendly Biodegradable Polymers and Composites. Integrated Waste Management” - Volume I, ed. S. Kumar. 2011.
- [2] R.S.Blackburn,,ed. “Sustainable textiles Life cycle and environmental impact”, Woodhead Publishing in Textiles: Great Abington Cambridge, UK.,2009.
- [3] A.A.a.E Pollet,,ed, “Environmental Silicate Nano-Biocomposites”, Green Energy and Technology. Springer Verlag, London ,2012.
- [4] R.W.A Abdul Razak, Wan Abdul Rahman, Lee Tin Sin, ed. “PLA Biopolymer Technology and Applications”, Polylactic Acid, ed. S. Ebnasajjad, Elsevier Inc. PDL Handbook Series: Chadds Ford, PA, USA, 2012.
- [5] L.A.a.E Pollet, “Biodegradable Polymers, in Environmental Silicate Nano-Biocomposites”, Green Energy and Technology, L.A.a.E. Pollet, Editor, Springer: Verlag London, 2012.
- [6] A.Steinbuchel, “Biopolymers, general aspects and special applications”, Wiley-VCH: Weinheim, 2003.
- [7] A.Richard, G.a.B.K, “Biodegradable Polymers for the Environment”, in Science Magazine - www.sciencemag.org, Aug - 2002.
- [8] D.L. Kaplan, M.J. Ball D, J.McCassie , A.L Allen, P.Stenhouse, “Fundamentals of biodegradable polymers in Biodegradable polymers and packaging”, K.D. Ching C, Thomas EL, Editor., Technomic Pub Co: Lancaster, pp. 1-42, 1993.
- [9] K.K.P Van de Velde, K, “Biopolymers: overview of several properties and consequences on their applications” Polym Testing.,21(4), pp. 433-442, 2002.
- [10] A.R.L Rouilly, “Agro-materials: A bibliographic review. Journal of Macromolecular Science”, Part C: Polymer Review C, 42(4): pp. 441-479, 2002.
- [11] A.Guilbot, M.C., “The polysaccharides, in Molecular biology”, A. GO, Editor. 1985, Academic Press Incorporation: New York. pp. 209-282.
- [12] G.Della Valle, B.A., P.J.Carreau, P.A.Lavoie, B.Vergnes, “Relationship between structure and viscoelastic behavior of plasticized starch”,Journal of Rheology, 42(3), pp. 507-525, 1998.
- [13] P.Colonna, M.C., “Macromolecular structure of wrinkled- and smooth-pea starch components.Carbohydrates”, Research, 126(2): pp. 233-247. 1984.
- [14] S.T.Y.Hizukuri, M.Yasuda, “Multi-branched nature of amylose and the action of debranching enzymes.Carbohydrate Research”, 94(2): pp. 205-213, 1981.
- [15] A.Hayashi, K.K., Y.Miyake, Cho CH, “Conformation of amylose in solution”, Polym Journal, 13(6): pp. 537-541,1981
- [16] A.N.C.Netravali S, “Composites get greener Materials Today”, 6, pp. 22-29,2003.
- [17] R.R.R.Chandra,“Biodegradable polymers”. Progr.Polym.Sci, 23: pp. 1273-1335,1998.
- [18] R. A. Gross, J.-D.G., D. Eberiel, S. P. McCarthy, “Pure applied Chemistry”, Journal of Macromolecular Science, 613(A32) ,1995.
- [19] C. M. Buchanan, B.G.P., A. W. White, M. D. Wood, “Polymer Degradation. Journal of Environment”, 209(5), 1997.
- [20] C. M. Buchanan, B.G.P., A. W. White, M. D. Wood, “Polymer Degradation”, Journal Environment, 179(4),1996.
- [21] W.L.K Teng, E. Tan, T.K.; Lim, L.Y.; Tan, S.C, “Concurrent production of chitin from shrimp shells and fungi Carbohydrates” Research, 332: pp. 305-316, 2001.

- [22] V.K.Thakur, M.K. Thakur, "Handbook of Sustainable Polymers: Structure and Chemistry", Pan Stanford Publishing.
- [23] S.Y.L Park, B.I. S.T. Jung, J.H. Park, "Biopolymer composite films based on carrageenan and chitosan", *Material Research Bulletin*, 36, pp. 511-519, 2001.
- [24] Muzzarelli, R.W., M. ;Bicchiega, V, N-carboxybutyl chitosan as a wound dressing and a cosmetic ingredient. *Chim.Oggi*, 9: pp. 33-37, 1991.
- [25] R.P.M.Jayakumar, R.L.Reis, J.F. Mano, "Graft copolymerized chitosan-present status and applications. *Carbohydrate*" *Polymers*, 62: pp. 142-158, 2005.
- [26] R.N.N.Jayakumar, S.Tokura, H.Tamura, "Review Sulfated chitin and chitosan as novel biomaterials. *International Journal of Biological Macromolecules*", 40, pp. 175-181, 2007.
- [27] R.S.N.Jayakumar, S.V.Nair, S.Tokura, "Tamura, S, Preparative methods of phosphorylated chitin and chitosan -An overview, *International Journal of Biological Macromolecules*", 43: pp. 221-225, 2008.
- [28] L.T.Isabelle Vroman, "Biodegradable polymers. materials", *www.mdpi.com*, 2, pp. 38, 2009.
- [29] R.R.R.Chandra, "Biodegradable polymers", *Progr. Polym. Sci*, 2, pp. 38, 1998.
- [30] L.Z.M.Zhang, "Proteins as sources of materials, in *Monomers polymers and composites from renewable resources*", G.A. Belgacem M, Editor. Elsevier: Amsterdam. pp. 479-493, 2008.
- [31] C.S.M.Gao, N. Wellner, "Plasticization of a protein-based film by glycerol: A spectroscopic, mechanical, and thermal study", *Journal of Agriculture Food Chemistry*, 54, pp. 4611-4616. 2006.
- [32] Y.Z.Song, "Quality Improved tensile strength of glycerol-plasticized gluten", *Bioresource Technology*, 99: pp. 7665-767, 2008.
- [33] K.P.Gelse, E.; T.Aigner, "Collagens - Structure, Function and Biosynthesis", *Advanced Drug Delivery Review*, 55, pp. 15, 2003.
- [34] L.S.L.Nair, C.T., "Biodegradable polymers as biomaterials", *Progr. Polymer Science*, 32, pp. 38, 2007.
- [35] L.L.H. Madison, G.W., "Metabolic Engineering of poly(3-hydroxyalkanoates): from DNA to plastic *Microbiological Molecules*", *Biological Review*, 63, pp. 21-53, 1999.
- [36] O.Masahiko, "Chemical syntheses of biodegradable polymers", *Prog. Polymer Science*, 27, pp. 87-133, 2002.
- [37] S.Mecking, "Nature of petrochemistry? *Biologically degradable materials*", *Angew. Chem. Int. Ed*, 43, pp. 1078-1085, 2004.
- [38] J. E. Potts, R.A.C. W. B. Ackart, W. D. Niegish, "Biopolyester synthesis by enzymatic catalysis and development of nanohybrid systems", *Polym. Sci. Technol*, 61 (3), 1973.
- [39] Y. Tokiwa, T.A., T. Suzuki, "Chemical and physical changes occurring in polyester polyurethane during biodegradation", *Journal of Fermentation Technology*, 603(54), 1976.
- [40] W. J. Cook, J.A.C. J. P. Bell, S. J. Huang, *Polymer Letter Ed.*, "Hand book of biodegradable polymers", *Journal of Polymer Science*, 19(159), 1981.
- [41] D.E.A. Anderson, "Occurrence, metabolism, metabolic role and industrial uses of bacterial polyhydroxyalkanoates", *Microbiol Review*, 45: pp. 450-472, 1990.
- [42] G.Q.Chen, W.Q., K.Zhao, H.P.Yu and A.Chan, . Chinese, "Chiral biopolyesters- polyhydroxyalkanoates synthesized by microorganisms", *Journal of Polymer Science*, 18: pp. 389-396, 2000.
- [43] G.Q.Chen, K.K.a.L.R., "Production of poly-D(-)-3-hydroxybutyrate and poly-D(-)-3-hydroxyvalerate by strains of *Alcaligenes latus*", *Antonie van Leeuwenhoek*, 60, pp. 61-66, 1991.

- [44] G.Q.Chen, Z.G. S.J.Park, S.Lee, “Industrial Production of Poly(hydroxy- butyrate-co- hydroxy- hexanoate)”, *Appl MicrobiolBiotechnol*, 57(57), pp. 50-55,2001.
- [45] Y.Tokiwa, S., “Hydrolysis of polyesters by lipases”, *Nature*, 270(5632), pp. 76-78,1977.
- [46] S.R.Lee, P.H.-M., H. Lim, T. Kang, X.Li, W.J.Cho, Ha “Microstructure, tensile properties, and biodegradability of aliphatic polyester/clay nanocomposites”, *Polymer*, 43(8), pp. 2495-2500, 2002.
- [47] R.J.MullerW.U, E.Rantze, W.D.Deckwer “Architecture of biodegradable copolyesters containing aromatic constituents”, *PolymDegrad Stab*, 59(1-3), pp. 203-208, 1998.
- [48] D.K.Platt, “Biodegradable Polymers, Rapra Technology”, *Smithers Rapra Limited, Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK,2006*,
- [49] T.A.R.Keshavarz, “Polyhydroxyalkanoates: bioplastics with a green agenda”, *Current Opinion on Microbiology*, 13, pp. 321 – 326,2010.
- [50] G.M.F.Aragao, W.Schmidell, J.L.Ienczak, and Fischer, PCT - WO2009/149529 “A1-Preparation of polyhydroxyalkanoates” from a citric residue, S.A, 2009.
- [51] F.Dalcanton, J.L.Ienczak, M.L.Fiorese and G.M.F.Aragao, “Production of poly(3-hydroxybutyrate) PorCupriavidusnecatoremmeio hydrolysis of amino de arroz com suplementscas de ó leo de soja at different temperatures”, *Quím, Nova*, 33(3), p p. 552 – 55, 2010.
- [52] S.P.SohelRana, P.Shama arveen and Raul Fanguero, ed. “Biosynthetic Fibers: Production, Processing, Properties and Their Sustainability Parameters”, *Roadmap to Sustainable Textiles and Clothing*, ed. S.S. Muthu, *Textile Science and Clothing Technology: Springer Science and Business Media Singapore*, 2014.
- [53] John Summerscales, P.J.Nilmini, Dissanayake, Amandeep S.Virk,WayneHall, “A review of bast fibres and their composites”, Part 1 – Fibres as reinforcements”, *Review, Science Direct, Volume 41, Issue 10*, pp. 1329-1335, October 2010.
- [54] D.W.Farrington, D.J., Blackburn RS ed. “Poly (lactic acid) fibers”, In: *Biodegradable and sustainable fibers*, ed. B.R.S, Woodhead Publishing Ltd: Cambridge. pp.191-192, 2005.
- [55] S.Solarski , F.M. E.Devaux , “Characterization of the thermal properties of PLA fibers by modulated differential scanning Calorimetry”, *.Polymer*, 46, pp. 11187-11192, 2005.
- [56] J.Lunt, “Poly (lactic acid) polymers for fibers and nonwovens”, *International Fiber Journal*, 1, pp. 48-52, 2000.
- [57] R.S.Blackburn, ed. “Biodegradable and sustainable fibres”, *Woodhead publishing in Textiles*, 2005.
- [58] Vaeovan Saicheua, Tim Cooper, Alistair Knox, “public understanding towards sustainable clothing and the supply chain”,*Core UA Metadata,Septmber,2011*.
- [59] H. Benninga, ed. “A history of lactic acid making”, *Springer, New York*1990.
- [60] W.A.D.Yunzi Hu, Kevin Ka Leung Cheuk, and Carol Sze Ki Lin, “Newly developed techniques on polycondensation, ring-opening polymerization and polymer modification: focus on Poly(Lactic acid)”, *Materials*, www.mdpi.com, 133(9), 2016.
- [61] P.R.H. Gruber, E.S. Kolstad, J.J. Iwen, M.L. Benson, R.D. Borchardt, R.L., “Continuous process for manufacture of lactide polymers with controlled optical purity”, *Google Patents*, 1992.
- [62] P.G.a.M.O.Brien, ed. *Polyester III – “Applications and commercial products. In Biopolymers”*, Vol. 4, 235, *Wiley-VCH: Weinheim*, 2002.
- [63] Ozan Avinc, Akbar Khoddami, Hossein Hasani,

- “A mathematical model to compare the handle of PLA and PET knitted fabrics after different finishing steps”, *Fibers and Polymers*, volume 12, no.405,2011.
- [64] M. MirafTAB, H.A.R., ed. “Ecotextiles: The way forward for sustainable development in textiles”, Woodhead Publishing Limited, Cambridge England: CRC Press Boca Raton Boston New York Washington DC, 2007.
- [65] M. MirafTAB, A. R. Horrocks, “Ecotextiles: the way forward for sustainable development in textiles, (Woodhead Publishing Series in Textiles)”, W.H.B, ISBN-13, 978 - 1845692148, Feb, 2007.
- [66] G.F.S.S.M Moore, “Advances in Biodegradable Polymers”, *Rapra Review Reports*, vol. 9, no. 2, 1997.
- [62] Yaobang, Luwang, Hailian Zhang, Zhiyong Qian, “Stabilization and mechanical properties of biodegradable aliphatic polyesteamide and its filled composites”, *Polymer Degradation and Stability*, 83, pp 87-92, May, 2003.
- [68] H.H. Chuah H.S. Brown, and P.A. Dalton, (A) “Poly(trimethylene terephthalate): A new performance fiber”, *International Fiber Journal*, October, 1995.
- [69] H.H. Chuah, F.Werny, and T.Langley, “Dyeing and staining of Poly (Trimethylene Terephthalate) Carpets”, *International Conference and Exhibition of the American Association of Textile Chemists and Colorists*, 1995.
- [70] W.A. Dickson, “Improvements relating to the manufacture of highly polymeric substances” - British Patent 578,079, U.S. Patent 2,465,319. *Polymeric Linear Terephthalic Esters*-194, 1949.
- [71] F.A.C. Werny, H. H, “PTT - A new polyester for the carpet industry: An overview of extrusion, texturing, twisting and the effects of heat-setting”, C.a.R. Industry, Editor. May/June, 1996.
- [72] A. Anton, “Piece-dyeing for style and performance”, *Textile Chemist and Colorist & American Dyestuff Reporter*, 2000.32(3): p. 26-32.
- [73] Y.Q.Yan., S.Li. Q, H. Brown, and P.Casey, “Dyeing behavior of 100% poly(trimethylene terephthalate) (PTT) textiles”, *Textile Chemist and Colorist & American Dyestuff Reporter*, 1, pp. 50-54, 1999.
- [74] L.R. Lynd, C.E.W, T.U. Gerngross, “Toward low-cost biological and hybrid biological / catalytic conversion of cellulosic biomass to fuels”, *Biotechnol. Prog.*, 15(777), 1999.
- [75] J. Lunt, “Large-scale production, properties and commercial applications of polyactic acid Polymers, *Polymer Degradation and Stability*, Vol. 59, Issue 1-3, pp 145-152, Jan, 1998.
- [76] G.Q Chen, “Industrial Production of PHA”, *Plastics from Bactena*, Vol.14, ISBN, 978-9-642-03286-8, 2010.
- [77] Fact.MR, Industry Report on “Polycaprolactone market on chemical and materials”-Regional Forecast 2021-2031, Nov, 2021.
- [78] Fortune Business Insights, Industry Report on “Plastics polimers & resins for the base year 2020”, March, 2021.