Sustainable Biopolymers in Textiles: An Overview

T. Karthik and R. Rathinamoorthy

Contents

Introduction ..................................................................................... 1436
Need for Alternative Material ........................................................... 1437
Biopolymers .................................................................................. 1437
  Biopolymers from Natural Resources: Polysaccharides ...................... 1440
  Biopolymers from Natural Source: Animal Protein ............................ 1440
  Regenerated Fibers ...................................................................... 1443
  Biopolymers from Microorganisms ................................................. 1448
  Biopolymers from Bio-Derived monomers ....................................... 1449
  Sustainable Polyester Fibers .......................................................... 1451
Conclusions and Recommendations for Going Forward .................... 1455
References ...................................................................................... 1457

Abstract

Biopolymers are polymers synthesized by living organisms. Biopolymers can be poly-nucleotides such as the nucleic acids DNA and RNA, polypeptides, or polysaccharides. These consist of long chains made of repeating, covalently bonded units, such as nucleotides, amino acids, or monosaccharides. Biopolymers can be sustainable, carbon neutral, and are always renewable, because they are made from plant materials which can be grown indefinitely. Therefore, the use of biopolymers would create a sustainable industry. This chapter details the four different biopolymers which are likely from the natural resources and also from the synthetic pathways. The first method discussed is agro products which are

T. Karthik
Department of Textile Technology, PSG College of Technology, Coimbatore, Tamil Nadu, India
e-mail: peacesoul123@gmail.com

R. Rathinamoorthy
Department of Fashion Technology, PSG College of Technology, Coimbatore, Tamil Nadu, India
e-mail: r.rathinamoorthy@gmail.com

© Springer Nature Switzerland AG 2019
L. M. T. Martínez et al. (eds.), Handbook of Ecomaterials,
https://doi.org/10.1007/978-3-319-68255-6_53
obtained by the different natural biomass like polysaccharide, plant and animal protein with their properties and application areas. The second type of biodegradable fiber conferred is fibers extracted from microorganisms. The other kind of materials spotlighted is synthesis method both from the biologically derived biomonomers and also by the routine synthetic monomers. All the fibers were detailed for their special properties and potential application areas in our day-to-day life.

**Keywords**
- Sustainability · Luxury · Biopolymer · Spider silk · Hagfish slime · Seaweed · Milk fiber · PLA · PTT

**Introduction**

According to UN world commission on Environment & Development, sustainability is defined as “meeting the needs of the present without compromising the ability of future generations to meet their own needs” [1]. In other words, sustainability is development for environmental, economic, and social well-being for today and tomorrow. Sustainable development insist on minimizing the adverse impact on the quality of air, water, and other natural resources so as to sustain the ecosystem’s overall integrity.

Since the textile industry is one of the major contributors of environment pollution, sustainability becomes the vital factor in the textile value chain toward production of environment friendly and sustainable products to their customers as well as to preserve the environment for the future [2, 3]. The reduction of carbon footprint in textiles can be minimized by understanding the utilization of renewable biomass. Burning of fossil fuels and deforestation resulted imbalance of carbon cycle leading to release of massive quantity of CO2 to the atmosphere, which cannot be completely compensated by photosynthesis process or dissolution in the oceans [4, 5]. The consumers are now more aware about the GHG emissions and about the environment and hence the use of renewable resources should be considered for the sustainable development.

The challenge for the textile industry is in the areas of fiber, yarn and fabric production, textile chemical processing, garment making-up, transportation, use of products, recycling of textiles, and disposal of clothing. The synthetic fibers are generally dominant over the natural fibers due to their superior properties, but the low cost of synthetic fibers cannot be assured in future due to the ever demanding raw material, energy, and transportation costs [6, 7]. The majority of synthetic polymers are produced from petrochemicals which are nonbiodegradable in nature. Hence, the major challenge toward synthetic fiber manufacturing sector is the production of eco-friendly fibers with concern over environmental degradation [6, 8–10]. In case of synthetic fiber manufacturing industry, sustainability aspects are primarily focused on lessening the GHG emissions during the production and increasing the lifetime of synthetic textile products by means of recycling and reuse.
These restrictions in currently available natural and synthetic fibers lead to the development of biopolymers/biodegradable polymers/green polymers, which are either polymers occurring in living organisms with a specific biological function or plastic materials that are made from renewable resources or polymers which disintegrate by microorganisms or polymers which promote environmental sustainability during their life cycle. Biopolymers offer significant positive impact by reducing the dependence on fossil fuels and reduced carbon dioxide emissions. A raw material from biopolymers gives a greater scope as it combines both technical potentialities and sustainability. They are polymeric materials derived from raw materials for biological provenance [11]. Biopolymers are different from biodegradable and green polymers. Biodegradable polymers are one that breaks down into smaller fragments due to the action of bacteria and other microorganisms. Green polymers, on the other hand, are those produced using green (or sustainable) chemistry, a term that appeared in the 1990s. This chapter aims to provide brief insight into the biopolymer fibers, which will have massive impact on sustainable textiles in future.

**Need for Alternative Material**

The environmental impacts of commonly used natural and synthetic fibers are given in Table 1.

Cotton growing and harvesting requires huge amount of pesticides, water, and need large quantities of chemicals for processing and dyeing. Regenerated cellulosic fibers such as rayon or viscose are made of cellulose extracted from trees, but they also need chemical for processing it to a useful polymer. Synthetic fibers such as polyester, nylon, acrylics, etc., basically hugely rely on nonrenewable petroleum sources for their production. Thus, there is a major impact of such polymers on environment. From economic point of view, decreasing oil resources is likely to increase oil prices, skyrocketing energy cost, etc., prevails. Thus in recent years, we are experiencing the need for renewable polymers and a major thrust toward the development of biobased materials. There is paradigm shift from petro-chemistry to green chemistry. Green chemistry concept was developed since 1960s but implemented in 1990s. Green concept focuses to minimize the environmental impact of manufacturing processes through careful management of feedstocks, energy, waste, and products [13–15].

**Biopolymers**

Bio-based polymers are materials that are derived from renewable resources [16, 17]. The first generations of biopolymers are polymers derived from agricultural feedstocks such as corn, potatoes, and other carbohydrate sources. But in recent years, focus is shifted from food-based resources due to significant breakthroughs in biotechnology [11, 18]. The classification of biopolymers based on the process of synthesis is shown in Fig. 1.
Polymers from biomass. For example, agro-polymers derived from agro-resources such as cellulose or starch. Polymers obtained from microorganisms like polyhydroxyalkanoates (PHAs). Polymers obtained by conventional synthesis process using monomers derived from agro-resources, e.g., the polylactic acid (PLA). Polymers obtained from fossil resources.

In a daily life, polymers produced from fossil resources such as polyethylene, polypropylene, polyester, and polyvinylchloride are used in large quantities and other polymers in smaller quantities [19–22].

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Whether nonpolluting to obtain, process, and fabricate?</th>
<th>Produced from renewable resources?</th>
<th>Biodegradable?</th>
<th>Reusable/recyclable?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>No Fertilizers, herbicides, pesticides, dyes, and finishing chemicals used can pollute air, water, and soil</td>
<td>Yes Cotton comes from cotton plants that are renewable</td>
<td>Yes</td>
<td>Yes But it is difficult to recycle cotton from postconsumer products</td>
</tr>
<tr>
<td>Wool</td>
<td>No Runoff contamination, chemicals used for cleaning, dyeing, and finishing can cause pollution</td>
<td>Yes Wool comes from sheep, which are renewable</td>
<td>Yes</td>
<td>Yes Wool can be recycled</td>
</tr>
<tr>
<td>Rayon</td>
<td>No Harsh chemicals used to process wood pulp, and dyes and finishing chemicals can cause pollution</td>
<td>No Wood pulp used for rayon comes from mature forest</td>
<td>Yes</td>
<td>Yes Rayon fibers have not been recycled</td>
</tr>
<tr>
<td>Tencel®</td>
<td>No Chemicals used for dyeing and finishing can cause pollution</td>
<td>Yes Trees used for Tencel® are replanted</td>
<td>Yes</td>
<td>Yes Tencel® has not been recycled</td>
</tr>
<tr>
<td>Polyester</td>
<td>No Chemicals used for dyeing and finishing can pollute air and water</td>
<td>No Petroleum sources are not renewable</td>
<td>No</td>
<td>Yes 100% polyester has been recycled</td>
</tr>
<tr>
<td>Nylon</td>
<td>No Chemicals used for dyeing and finishing can pollute air and water</td>
<td>No Petroleum sources are not renewable</td>
<td>No</td>
<td>Yes 100% nylon has been recycled</td>
</tr>
</tbody>
</table>

Table 1 Environmental impacts of important natural and synthetic textile fibers (Source: Karthik and Gopalakrishnan [12])
Bio-polymers

Biomass products
(Agro polymers)

Polysaccharides
• Starches
  • Wheat, Potatoes, Maize etc.
  • Ligno-cellulosic products
  • Wood, Straws etc.
• Plant Proteins
  • Zein, Soya, Gluton

Proteins, Lignin...

• Animal Proteins
  • Casein, Whey, Collagen, Gelatin

PolyHydroxy-Alkanoates (PHA)
• Poly(hydroxybutyrate) (PHB)
• Poly(hydroxybutyrate co-hydroxyvalerate) (PHBV), etc.

Polylactides
• Polylactic acid (PLA)

From Micro-organisms
(Obtained by extraction)

From Bio-technology
(Conventionally synthesised from bio-derived monomers)

From Petrochemical products
(Conventionally synthesised from synthetic monomers)

Polylactides

• Polycaprolactones (PCL)

Others homo-polyesters

Aliphatic co-polyesters

Aromatic co-polyesters

Fig. 1 Classification of biopolymers
Biopolymers from Natural Resources: Polysaccharides

Polysaccharides are the complex carbohydrates which form the structural elements of plants and animals and are abundant in nature [11, 18]. Various polysaccharides from which biopolymers can be synthesized are as follows:

- Starch: Extracted from wheat, corn, and potatoes
- Chitin and chitosan: Crystalline microfibrils forming structural components in exoskeleton of arthropods or in the cell walls of fungi and yeasts
- Pectin

Starch is an important polysaccharide and is the most abundant in nature and relatively inexpensive. Natural starch normally exists in granular form and it can be used as filler in polymers or otherwise it can be processed with conventional plastic processing technologies. The main drawback in the usage of starch is its hydrophilic property, which limits its application in high moisture environments [23]. Starch can be blended with PVA, PCL, chitosan, derivatives, and other degradable polymers to produce fully biodegradable materials. Further, application of starch can be explored for drug delivery carriers in tissue engineering applications, as microcellular foams and in food industry [24–26].

Chitosan, the most significant biopolymer, is derived by deacetylation of chitin and is finding applications for the development of drug delivery systems owing to its biocompatibility, biodegradability, low toxicity, as well as abundant availability and low production cost [27, 28]. The production of chitosan from crustacean shells, seafood industry wastes, is still economically feasible. One of the major drawbacks of chitosan-based materials is its inferior mechanical strength. Because of reactive amino and hydroxyl functional groups, chitosan is frequently blended with other polymers to enhance their functional properties by means of inter- or intramolecular crosslinking in the polymer matrix.

Cellulose is another significant biopolymer available in abundant and is found in the cell walls of plants. It has some promising properties, such as mechanical robustness, hydrophilicity, biocompatibility, biodegradability, relative thermostability, high sorption capacity, and alterable optical appearance [29, 30]. The application of cellulose has been found in many areas. The production of bio-composites from cellulose is one of them as it offers great advantages.

Biopolymers from Natural Source: Animal Protein

Proteins are polypeptide-based polymers formed by condensation polymerization of amino acids. Collagens, casein, fibroin, and keratin are the important animal proteins. Proteins play a critical role as building blocks of many complex hierarchical biological material scales. Collagen, another biomaterial, is abundantly available as protein in extracellular matrices of vertebrate animals and has found major applications in biomedical field [18]. Collagen normally exists in the form of fibrils which
provide the main mechanical support and structural organization of connective tissues. Owing to its structure along with its biocompatibility and biodegradability, they are mostly found in applications fields such as tissue engineering applications, wound healing, and in cosmetics [31].

The major challenge in the research and development filed in the field of bio-polymers is to propose suitable modification techniques to enhance the properties of natural polymers. One such example is the development of wheat proteins or wheat gluten based natural polymers. Wheat gluten, a by-product of the starch industry with high protein content, could be considered suitable for lots of applications because of its good thermoplastic properties, good processability, and its remarkable biodegradability.

**Spider Silk**

Spider silk is a natural protein fiber and has better mechanical properties than silkworm silk. This is mainly due to the fact that the silkworm uses the silk for protection during metamorphosis, while spider silk uses their silk to catch the prey [32]. Spider silk has been recognized as fiber with unique combination of high strength and rupture elongation. In 1950s, spider silk in specific dragline silk attracted the focus of material scientist owing to their outstanding mechanical properties which can outperform any natural or synthetic fibers.

The golden orb spider and the spinneret in it are shown in Fig. 2. Spider silk proteins are synthesized from specialized abdominal glands that function as bio-factories to produce large quantities of silk fibroins which are spun into silk with different properties, composition, and morphologies [33].

**Production of Spider Silk**

The spiders have different glands to produce the different types of silk. Spiders produce silk by a process called “pull-trusion.” Unlike “extrusion” in which fiber is squeezed out of a reservoir, the spider pulls the finished thread directly from the silk-making gland. Large scale of production of spider silk is difficult which is hindering the growth of using spider silk in many applications. Spider silk is still in the very early stages, and it may be decades before it can be put into actual applications [33, 34]. However, there are lots of research groups who are focusing on development of

![Fig. 2 Golden orb spider silk species and the spinneret of spider silk (Source: http://www.chm.bris.ac.uk)](http://www.chm.bris.ac.uk)
Technical for mass productions of spider silk [33]. The efforts to reproduce spider silk have encountered many innovative methods and materials ranging from genetic modification to recycled silk to stem cells with many success and limitations [35, 36].

Traditional Methods: Spiders are highly territorial and aggressive creatures; hence, it is not possible to raise spiders together in the same environment. In order to collect spider silk directly from spiders, these would have to be captured from the wild and housed individually. *Nephila clavipes*, a golden orb-weaving spider, has been studied extensively by numerous groups worldwide because it is a larger spider, which makes routine operations and handling a little bit easier.

Artificial Biosynthesis: Researchers have developed methods to artificially produce the liquid silk precursor using other organisms. Some of these methods are discussed below.

- Chimeric silkworms – Normally, the postproduction spinning technologies has to be used like extrusion in order to convert the liquid monomers into silk fibers; however, these techniques are not yet reliable or effective. One requirement of this method of production is that silkworms still produce endogenous silk proteins, thus the resulting product is actually a combination of both silkworm and spider silk fibers.
- Transgenic goats – Mammal cells have also been used as a host to produce spider silk monomers.
- Metabolically engineered *Escherichia coli* – Using *E. coli* as an expression system to produce spider silk proteins of similar molecular weight and mechanical properties as native spider silk was reported.

Applications of Spider Silk

If the production of spider silk ever becomes industrially viable, it could replace Kevlar and can be used in diverse range of applications such as [34, 37]:

- Bullet-proof clothing
- Wear–resistant lightweight clothing
- Ropes, nets, seat belts, parachutes
- Rust-free panels on motor vehicles or boats
- Biodegradable bottles
- Bandages, surgical threads
- Artificial tendons or ligaments, supports for weak blood vessels

Hagfish Slime Fibers

The hagfish are snake-like creatures that live on the bottom of the ocean. Hagfish are known for their ability to produce large volume of slime when they are provoked or stressed as a defensive mechanism. Hagfish produce a mucus-like, viscous substance from their body when startled. This slime is composed of mucins and seawater, held together by long protein threads [38].

The slime threads have an α-keratin like intermediate filament (IF) structure and thread bundles are aligned 1–3 μm in diameter and are several centimeters long. The
formation of these bundle of fibers is unique as shown in Fig. 3 and consists of following steps: Individual α-helices form coiled-coil dimers (A) that self-assemble into subfilaments, that in turn form complete IF (B) of 10 nm in diameter that align to form one continuous macroscopic fiber (C). This process occurs entirely within a single gland thread cell (GTC) and does not stop until the entire cell is completely filled with this newly formed fiber. Upon ejection out of the glands, individual GTC lose the thin membrane that coated them (D & E) [40–42].

Slime threads and constituents intermediate filaments possess a number of attractive properties that make them promising protein fibers along with spider silk. The threads that are stretched in water and dried have excellent material properties. These threads resemble dragline spider silk in the super molecular structure aspects [43]. Lot of researchers working on the analysis, production of Hagfish slime and it is not far that the fibers will available in useful form. When stretched in water and dried, it resembles silk and soon will release synthetic fibers like nylon and polyester in many applications. Researchers indicate that Hag fish slime threads will be a candidate of high performance eco-friendly clothing and will be fashion for future and also might be used for stockings or breathable athletic wear or even bullet-proof vests or ballistic protection [38].

**Regenerated Fibers**

Regenerated fibers are manufactured artificially by using the building blocks provided by nature (e.g., proteins or cellulose) compared to fibers made entirely by nature. They can be categorized as regenerated fibers from cellulose and regenerated fibers from proteins.

**Biofibers from Regenerated Cellulosic Fiber**

Rayon, the first regenerated cellulosic fiber, became popular due to shortage of natural fibers, availability of renewable forest resources, and relatively low cost. On the other hand, development of cheaper synthetic fibers, use of carbon disulfide in rayon manufacturing, as well as depletion of forest resources led to fall of first generation regenerated cellulosic fibers. But an environmentally friendly lyocell process based on N-methylmorpholine-N-oxide monohydrate...
solvent system is being developed for the manufacturing of regenerated cellullosic fiber [44]. Among the regenerated cellullosic fiber, seaweed fiber is widely considered and researched for raw materials as a textile fiber material due to biodegradability, health benefits, etc.

**Seaweed Fiber**

After an intensive research work, Zimmer AG has developed a seaweed based fiber known as SeaCell®. It is produced using an innovative lyocell technique in which seaweed containing vitamins, minerals, and trace elements are added to the cellulosic pulp before the spinning process [45–47].

The manufacturing process is illustrated in Fig. 4. Seaweed mainly from the family of brown, red, green, and blue algae is used for the manufacture of sea cell fibers. Coarse crushed seaweed material is processed to fine seaweed powder by specialized milling technology. The seaweed/algae are added either as a powder form or as suspension in one of process steps preceding the spinning of the cellulose solution. In the lyocell process, the cellulose is dissolved directly without formation of derivatives, as the solvent used is nontoxic, aqueous solvent N-methylmorpholine-N-oxide. The spinning solution is processed in a combined dry/wet spinning process.

![Fig. 4 Manufacturing process of SeaCell® active fibers [47]](image-url)
to form fibers and shaped cellulosic materials. During the spinning process, the solvent used in spinning solution is washed out and almost completely recovered.

The fiber can be used in fabrics and nonwoven material as 100% or as blends and yet retain their antimicrobial effects. These properties enable them to be used in wide range of applications [47]. Some of the applications include

- Workwear: Gloves
- Sportswear: Socks, yoga attire
- Underwear and lingerie
- Home textiles: Furnishings, beddings, filters, blankets
- Nonwoven materials and technical applications: Wipes, filters, and masks
- Household and hygiene applications: Baby clothings, towels, etc.

**Biofibers from Regenerated Protein Fiber**

Regenerated fibers from protein are called Azlons and sources of protein include soy, corn, peanut, and even milk. Azlon is produced by dissolving proteins like casein from milk, soy protein, zein from corn in dilute alkali and forcing the solutions through a spinneret into an acid-formaldehyde coagulation bath. These fibers resemble natural protein fibers but they suffer from low dry and wet strength and sensitivity to alkalis [48].

**Casein Fibers**

It is a new innovative fiber that has developed to compete with wool, which is a regenerated protein fiber made of casein from milk through bioengineering. Even though Milk fibers otherwise termed as casein fibers lack in some desirable properties of wool, it was a means to replace wool fibers at lower cost. Some of successful brands that developed milk protein fibers are (1) Aralac, America (2) Lanital, Belgium, France (3) Merinova, Italy, and (4) Fibrolane, Britain (www.swicofil.com). The various processes involved in production of milk fibers are given below [49, 50]:

- Extraction of raw materials – In order to extract casein protein, milk is first dewatered and skimmed and casein is obtained by the acid treatment of skimmed milk. The casein coagulates as a curd which is washed and dried and then ground to a fine powder.
- Polymerization – Casein is blended to minimize the effects of variation in quality, and then dissolved in sodium hydroxide. The solution is allowed to ripen until it reaches a suitable viscosity and is then filtered and deaerated.
- Spinning – Wet spinning technique is used by extruding the spinning solution through spinnerets into a coagulation bath consisting of two parts of sulfuric acid, five parts of formaldehyde, 20 parts of glucose, and 100 parts of water. The jet of solution coagulates into filaments similar to coagulation of viscose filaments. As the filaments emerge from the spinnerets, liquid polymer is converted to rubbery state and further it is solidified. The coagulated casein filament is very soft, weak, and can readily break. Hence, further processing is required so that the filaments can be successfully applied to textile applications.
• Crimping, cutting to staple fibers – After spinning, long staple filaments are cramped and cut into staple fibers.
• Hardening – Water can penetrate in fibers readily causing pushing apart long casein molecules and hence softening and swelling the filament. Hardening is done to minimize the softening effects of water.
• Washing, drying, and baling – After hardening, fibers are washed, dried, and packed to bales.

The milk protein fibers are silk like soft, glossy, lustrous, luxurious, and smooth to skin. It is hygroscopic in nature adding to comfortability. It is very easy to dye and can be dyed under normal temperature. Since it contains amino acid, it has antibacterial and antifungal characteristics. Milk protein fibers has excellent properties such as silk-like hand feeling, soft and elegant luster, wear resistance, stain resistance, moisture permeability, skin affinity characteristics, etc.

**Regenerated Protein Fibers from Bovine Serum Albumin (BSA)**

Bovine serum albumin was dissolved in water using dithiothreitol which acts as reducing agent at an acidic pH range of 4.7–5.0, and the resultant solution was poured onto glass plates. Further, the proteins were dehydrated at 30 °C and R.H of 30% and the fibers were formed by pulling the air over the solution at a constant rate which resulted in fibrillation. Recombinant human serum albumin (rHSA) proteins were also can be obtained by using transgenic silkworms having characteristics and structure similar to that of the native albumin. The DNA from HSA was introduced into silk glands through PiggyBac based transformation vector, and the glands were transplanted into larvae and reared to produce silk fibers.

**Regenerated Plant Protein Fibers**

Regenerated protein fibers were produced from cereal grains such as soy and peanuts in the 1950s. Regenerated fibers from peanut under the trade name Ardiil and proteins from corn zein marketed as Vicara and even from soybean were produced on a commercial scale and used for industrial applications.

The corn protein zein has been widely studied for fiber production because zein dissolves in aqueous ethanol solutions and has excellent spinnability. Zein fibers were prepared by using alcohol as a solvent with approximately 13–16.5% solids, in the pH range of 11.3–12.7. Chemicals such as urea were added to denature the proteins under heat. The fibers formed were coagulated using acids and salts, and in some cases formaldehyde was also used [51].

Soy isolates obtained from processing soybeans have also been used to produce fibers. The Ford motor company was probably the first to develop protein fibers from soy isolates as early as 1935. More recently, researchers at the Center for Crops Utilization Research at the Iowa State University have reported the properties of 100% SPF produced by extrusion and also by wet spinning. However, the process developed at the Iowa State University uses sodium hydroxide for dissolving the protein. Using an alkali such as sodium hydroxide hydrolyzes the proteins and reduces the degree of polymerization (DP) of the proteins [44].
Soybean protein fibers (SPF) are manufactured fibers, produced from regenerated soya *Glycine max* soybean proteins in combination with synthetic polymer (polyvinyl alcohol) as a predominant component. It is made from the soybean cake after oiling by new bioengineering technology. The main component of soybean fiber is it possesses the superiorities of many natural fibers and synthesized ones and it is quite similar to those of cashmere and silk, featuring fine denier, low density, and good tenacity and elongation. The manufacturing process of soybean fiber is presented in Fig. 5. Five main production stages can be identified:

1. Separation: “Clarifying” the soya bean meal and precipitating out the protein.
2. Solubilization: Dissolving the resulting washed and dried curd to form the “spinning” solution.
3. Hardening: Forcing this solution, when sufficiently ripened, through spinnerets into a coagulating bath resulting in the formation of fibers.
4. Insolubilizing: Stretching and hardening this fibers, often using formaldehyde.
5. Controlled washing and drying followed by cutting into staple lengths.

Pure (100%) soy protein fibers were developed and used for tissue engineering and controlled drug release applications. Soy proteins (26%) were dissolved in 8M urea and 1% sodium sulfite, and the solution was aged up to 96 h. After aging, the solution was extruded into a coagulating bath consisting of 10% acid and 10% sodium sulfate using a syringe and needle. Fibers obtained were drawn and annealed to improve tensile properties [52, 53]. Recently, protein fibers produced from soy isolates generally called SPF are reportedly available on the market (www.swicofil.com). However, the SPFs currently available on the market are not 100% SPF but are a blend of about 45% soy proteins and another synthetic polymer.
Biopolymers from Microorganisms

Polyesters are most widely used synthetic fibers and films in various fields, while plastic waste management recently became a critical problem of global environment. Among the various biomaterials poly-hydroxyalkanoates (PHA) play a significant role as plastic biopolymer produced from bacteria. These biopolymers represent family of intracellular biopolymers synthesized by bacteria as intracellular carbon and energy storage granules. They are mainly produced from renewable resources by fermentation. A wide variety of prokaryotic organisms accumulate PHA from 30–80% of their cellular dry weight. Depending on the carbon substrates and metabolism of the microorganisms, different monomers and thus co-polymers could be obtained. They are suitable for various applications such as short-term packaging, biocompatible in contact with living tissues, and can be used for biomedical applications [40–42].

In general, PHAs in its structure have several repetitions of the 150 different types of monomers which include units hydroxyalkanoates substituted with a wide range of groups such as alkyl, aryl, alkenyl, cyano, epoxy, ether, and acid groups. The structure and properties of PHA produced by microorganisms basically depend on the carbon source used. PHA are linear polymers of (R)-3-hydroxy acids in which the carboxyl group of a monomer forms an ester linkage with the hydroxyl group of the next monomer (Fig. 6).

PHAs are biodegradable polymers produced from a wide range of gram-negative and gram-positive bacteria that accumulate them in the cytoplasm, to act as storage materials, such as carbon, energy, and reducing power, that are manufactured by these organisms under unbalanced culture conditions [54]. For developing an effective process for the production of PHAs by fermentation technique, the use of microorganisms is unavoidable to optimize the performance and as well as the cost of the material used for their production. Bacterial synthesis of PHAs has been described in over 300 species. However, before the proper selection of microorganisms which are suitable for the industrial scale production, various factors to be considered are:

- The ability of the cell to grow on not very expensive carbon sources
- The speed or rate of growth
- The rate of synthesis of the polymer and
- The maximum possible polymer accumulated by the cell according to the available substrate

**Fig. 6** Molecular structure of PHAs

\[
\begin{align*}
&\text{R} \\
&\text{CH} \\
&(\text{CH}_2)_n
\end{align*}
\]
Polyhydroxybutyrate (PHB) and poly(hydroxybutyrate cohydroxyvalerate) (PHBV) are the most well-known polymers of the polyhydroxyalkanoates family. Their properties resemble that of synthetic plastics; however, the most attracting property of them is production and degradation which is contradictory to synthetic plastics. Polyhydroxybutyrate (PHB) is polyester from the PHA family and is accumulated by a wide variety of microorganisms as an intracellular storage source of organic carbon and chemical energy. For the organisms that can store, PHB is a primary assimilated carbon. When the cells are subjected to nutrient stress by using excess carbon with a deficient nutrient, synthesis of PHB occurs in cells. Other fermentation parameters like pH and temperature are physical factors that affect PHB production. Many species of bacillus are known to produce PHB [64]. The most studied are Alcaligenes eutrophus, Bacillus megaterium, Methylobacterium rhodesianum, M. extorquen, P. putida, and Sphaerotilus natans. The properties of the PHBV copolymer can be easily tailored by varying the valerate content.

Bacterial cellulose (BC) is another renewable natural material available in nano size which is characterized by superior mechanical properties, water absorbency, porosity, biodegradability, and excellent biological affinity. Bacterial cellulose possesses similar chemical formula of plant cellulose, but with distinctive three-dimensional porous cell-like structures. The bacterial cellulose has the following unique characteristics compared to plant cellulose:

(i) Absence of lignin and hemicellulose, which makes it a highly purified form of cellulose
(ii) High degree of polymerization combined with crystallinity (60–70%)
(iii) Extremely high water holding capacity (up to 100 times its weight)
(iv) Excellent biodegradability and biological affinity

In the last few years, growing worldwide activity can be observed regarding extensive scientific investigation and increasing efforts for the practical use of the BC materials. Functional BC-based nanomaterials are an attractive topic as they provide the creation of materials with improved or new properties by mixing multiple constituents and exploiting synergistic effects, such as electronic, optical, magnetic, catalytic properties, and bioactivity [29, 55].

**Biopolymers from Bio-Derived monomers**

Bio-based polyester is derived from natural resources using biotechnology. It includes poly lactic acid (PLA) and poly (trimethylene terephthalate) (PTT).

**Polylactic Acid (PLA)**

Polylactic acid (PLA) is the first melt-processable synthetic fiber produced from renewable resources, which combines ecological advantages with excellent performance in textiles. It is aliphatic polyester based on lactic acid \((\text{C}_3\text{H}_6\text{O}_3)\) and produced from the fermentation of agricultural resources. PLA requires 20–50%
less fossil resources and has the potential to reduce atmospheric CO₂ levels [56, 57]. Currently, Nature Works LLC, USA, is major supplier of PLA fibers under brand name Ingeo®, and other PLA fibers include Lactron® (KaneboGohsen Ltd), Ecodear® (Toray industries), Terramac® (Unitika), Plastarch® (Kuraray), etc. [58].

**Ingeo® PLA Fibers**
Cargill Incorporated has done the research work on lactic acid to develop the PLA technology and products to full commercialization. Trade name of PLA polymer is Nature Works® PLA and PLA fibers is Ingeo® fibers [56, 59–61]. The hydroxyl carboxylic acid (lactic acid monomer) is extracted from corn starch by converting starch to fermentable sugars through enzymatic hydrolysis process followed by bacterial fermentation. PLA could be produced by two routes such as polycondensation of lactic acid under high vacuum and high temperature and ring opening polymerization of a cyclic dimer of lactic acid [56, 57, 59, 61]. The first method involves the removal of water by condensation and utilization of solvent under high vacuum and temperature. But the limitation here is to get a high molecular weight PLA due to the formation of water during the process. On the other hand, the second method produces high molecular weight polymer, where the water is removed under milder conditions, without solvent to produce cyclic intermediate dimer referred to as lactide.

Cargill Dow LLC has innovated a low continuous process for the production of lactic acid based polymers. The process starts with a continuous condensation reaction of lactic acid to produce low molecular weight PLA pre-polymer. Pre-polymer is converted into mixture of lactide stereoisomers using tin catalysts to enhance the rate of intramolecular cyclization reaction. Finally, PLA polymer is produced using a ring-opening lactide polymerization eliminating the use of solvents. After the polymerization is complete, any remaining monomer is removed under vacuum and recycled to being used as raw material [57, 61].

**Lactron® – PLA Fibers**
Kanebo Inc. introduced a PLA fiber under the trade name Lactron® fiber. Lactron® is a PLA fiber which is made from lactic acid obtained through fermentation of cornstarch. It has the highest melting point of any biodegradable fiber ever developed, so it can be processed into multifilament, monofilament, staple fibers, or spunbonded fabrics suitable for any type of textile applications. It has fiber properties and processability comparable to those of conventional polyester and nylon. The weight of fibers decreases within a few years in soil followed by reduction in strength and ultimately decomposing the fibers leading to biodegradability. The main merit of using “corn fiber” or “PLA fiber” in applications is that it can solve the problem of dumping while keeping the advantages of conventional mixtures of synthetic and natural fibers [57, 58].

**Poly(Trimethylene Terephthalate)**
Polyester is a dominant synthetic fiber in apparel, home furnishings, and many other industrial applications. As an engineering thermoplastic, poly(trimethylene terephthalate) (PTT) has a very desirable property set and in terms of fiber, they
have good resiliency and wearability of nylon, as well as the dyeability and static and chemical resistance of PET [58, 62]. Though it has been synthesized in 1941 and having desirable properties, it has not been commercialized owing to its high cost of raw material (1,3-propanediol (PDO)). The DuPont have innovated a technique to produce Bio-PDO from corn sugar under the trade name “Sorona®, and targeting its applications on textiles, carpets, industrial fibers, and engineering plastics. It is corn-based fiber made from 1,3-propanediol (PDO) and a petrochemical-based monomer [22, 63, 64]. The production of Sorona® consists of two basic steps such as production of Bio-PDO and production of PTT from Bio-PDO.

The Bio-PDO has been produced by fermentation processes which consist of two stages, i.e., yeast ferment glucose to glycerol and microbes ferment glycerol to give PDO (Fig. 7). Then, PTT is produced either by transesterification process with dimethyl terephthalate (DMT) and Bio-PDO or by esterification route starting with purified terephthalic acid (PTA) and Bio-PDO.

The PTT has strength, stiffness, toughness, and heat resistance of polyester; processing parameters such as low melt and mold temperatures, rapid crystallization, faster cycle time as that of PBT; and good resilience and wearability as that of nylon. It also exhibits uniform dye uptake and with selected dyes, colorfastness comparable to nylon. It has excellent UV resistance, chlorine resistance, and low static charge generation [22, 63, 64]. Sorona® fibers can be used for various applications such as apparel, outdoor/sport goods, floor coverings, and as carpet fibers [63].

**Sustainable Polyester Fibers**

Polyesters are one of the most promising families of polymers due to their renewability, range of good properties, potential biodegradability, and also due to easy
accessibility of bio-based monomers for polyesters. As the polyester is a synthetic fibre, it is generally produced from petroleum resources, which are carbon-intensive nonrenewable resource. Polyesters are generally polymers where the monomers are linked to one another by means of ester groups. Some of the naturally occurring polyesters are shellac, cutin, and poly(hydroxybutyrate) (PHB), and synthetic polyesters are poly(ethylene terephthalate) (PET), poly(butylene succinate) (PBS), and poly(lactic acid) (PLA). Based on the main chain chemical composition, polyesters are classified as aliphatic, semi-aromatic, and aromatic polyesters. Aliphatic polyesters are generally sustainable as they are mostly produced from the biomass feed stocks [65, 66]. Further, they are biodegradable materials which can be recycled, disposed, or incinerated with minimum negative impact on the environment. Aromatic polyesters generally possess excellent mechanical, thermal, and chemical properties compared to aliphatic and semi-aromatic polyesters, and hence they are used in high-end application industries like chemical, electronic, aviation and automobile, etc. [67].

**Sustainable Bio-Monomers for Production of Polyester**

Biomass-derived monomers are generally categorized based on their natural molecular biomass origins. They are classified into four main types:

(i) Oxygen-rich monomers such as carboxylic acids, polyols, furans, and di-anhydro-alditols
(ii) Hydrocarbon-rich monomers such as fatty acids, vegetable oils, terpenes, terpenoids, and resin acids
(iii) Hydrocarbon monomers such as bio-propene, bio-ethene, bio-butene, and bio-isoprene
(iv) Non-hydrocarbon monomers such as carbon monoxide and carbon dioxide

Among the numerous sources of building blocks for synthesis of polyester fibres, lignin, carbohydrates, and vegetable oils, and to a lesser extent suberin, are the most interesting ones.

**Bio-Based Aliphatic Diacids**

Alditols, aldonic, and furans derived from monosaccharides through chemical or biological routes are needed for synthesis of aliphatic or aromatic monomers for polyester. The production of bio-based aliphatic diacids used for the production of polyester is discussed below. Itaconic acid (IA), an unsaturated dicarboxylic acid, was recognized for the first time during the thermal decomposition of citric acid in the year 1837. They are normally produced by fermentation method using fungi, which is more economical compared to thermal decomposition or chemical methods of production [68–70]. Adipic acid is normally found in nature in the juice of sugar and red beets, and the synthesis of adipic acid from renewable carbon sources like glucose derived from starch or cellulose is a likely alternative way for the synthesis of AA. On the other hand, biosynthesis of adipic acid can also be accomplished through α-amino adipate pathway or starting from long-chain carbon substrates [71, 72].
Succinic acid (SA) was obtained from amber distillation in the year 1546 by Georgius Agricola. During the process of fermentation, corn starch, cane molasses, whey, wood hydrolysates, and glycerol are generally converted into succinic acid by the action of particular strains of bacteria. Fumaric acid is a naturally occurring dicarboxylic acid and is first isolated from *Fumaria officinalis*. Fungi from *Cunninghamella, Rhizopus, Mucor,* and *Circinella* genera are capable to produce fumaric acid during fermentation of renewable raw materials at reasonable yields [73, 74]. Though fungi are the widely used microorganisms in the production of fumaric acid, few bacterial strains like *Lactobacillus ssp.* and metabolic engineered yeasts like *Saccharomyces cerevisiae* have also been used in the production of fumaric acid [74]. Dehydration of sugars in bio-refineries could result in set of products such as furans, dehydro sugars, and levulinic acid.

**Bio-Based Aliphatic Diols and Polyols**

The bio-based production of commonly used aliphatic diols and polyols are 1,3-propanediol (1,3-PDO), butanediol, glycerol, ethylene glycol, and sorbitol and isosorbide. Biological routes have been attempted for the production of bio-based 1,3-PDO using bacteria such as *Klebsiella pneumoniae, Lactobacillus brevis,* and *Enterobacter agglomerans* during anaerobic growth on glycerol [75]. Similarly, biomass-derived sugars such as lignocellulose or noncellulose, which are cheaper source, have been attempted for the production of butanediol [76].

**Bio-Based Aliphatic Diamines**

1,4-Butanediamine (1,4-BDA) could be synthesized naturally by the decomposition of amino acids in dead or living organisms. The bio-based 1,4-BDA can be synthesized through chemical conversion of biomass-derived succinic acid or by means of fermentation of sugars using *E. coli*. 1,5-Pentanediame (1,5-PDA), a natural compound, is synthesized by hydrolysis of protein during the tissue putrefaction of animals [77]. The bio-based synthesis of 1,5-PDA is carried out by decarboxylation of lysine using numerous microorganisms or fermentation of sugars using metabolic engineering. 1,6-Hexanediame (1,6-HDA) is a raw material for synthesis of nylon 6,6, nylon 6,10, and PA6,T, which is currently produced industrially from petrol-based butadiene or propylene [78]. Recent developments show that bio-based 1,6-HDA can be produced by chemical-catalytic conversion of adipic acid or 1,6-hexanediol derived from carbohydrates, or by a fermentation route. 1,8-Octanediame (1,8-O DA) can be potentially derived from biomass. It can be produced by amination of suberic acid which can be converted from plant oils. 1,10-Decanediame (1,10-DDA) can be chemically converted from sebacic acid derived from castor oils. They are interesting bio-based monomers for the synthesis of fully biobased nylon 10,10, which is already commercially available in the market [79].

**Vegetable Oil-Based Monomers**

Among the various vegetable oil-based monomers, ricinoleic acid extracted from the castor oil plays a significant role due to its bifunctionality. Poly(ricinoleic acid) can be prepared by lipase catalyzed condensation of methyl ricinoleate, which was
consequently cross-linked to produce thermosetting elastomers. This process has the advantage of utilizing both a renewable monomer and an eco-friendly synthesis approach. Moreover, poly(ricinoleic acid) can be easily recycled by enzymatic hydrolysis followed by re-polymerization.

In another research study, erucic acid has been tried for synthesis of monomer for the production of renewable aliphatic polyesters using olefin self-metathesis. Polycondensation of the resultant 1,26-hexacosanediolic acid with \( \alpha,\omega \)-diols produces the long-chain aliphatic polyesters with higher crystallinity, melting, and degradation properties [80]. In another study, use of thiolene and metathesis polymerization for the synthesis of aliphatic polyesters has also been reported by several researchers.

**Suberin and Cutin-Based Monomers**
The suberin and cutin monomers could also be explored for the production of bio-based aliphatic polyesters. Depolymerized suberin extracted from cork containing long-chain \( \alpha,\omega \)-dicarboxylic acids and \( \omega \)-hydroxy acids were used to synthesize the bio-based polyesters by emulsion polymerization. In another kind of study, depolymerized suberin extracted from cork as well birch outer barks along with functional groups like diols or diacids to balance the OH/COOH stoichiometry for the production of several interesting bio-based polyesters have also been explored [81].

**Sugar Diol-Based Monomers**
As the use of 1,4:3,6-dianhydrohexitols (DAHs) monomers like isosorbide, isomannide, and isoidide for the production of bio-polyesters resulted in advantages such as rigidity, nontoxicity, and sustainability, they have gained more important monomer for the synthesis of polyesters, but they have low molecular weight. Recent research in the production of bio-based aliphatic polyesters from DAHs is based on melt polymerization using renewable source of isohexide, wherein the isoiode dicarboxylic acid, diacid, and the isoidide dimethanol, diol were prepared by a multi-step process from isomannide [82]. On the other side, several interesting research works have been carried out on the production of bio-based polyesters from diols derived from sugars [83].

**Other Aliphatic Monomers**
Lactic acid is identified as a main metabolic intermediate and is currently produced in a chemical synthesis method through hydrolysis of lactonitrile, using concentrated hydrochloric acid. On the other hand, it can also be produced by means of bacterial fermentation of sugars, which requires the use of biomass feedstocks and need less energy consumption and low temperature.

3-Hydroxypropionic acid (3-HPA) can be synthesized using 1,3-PDO and 3-hydroxypropionaldehyde, but are costlier. Bio-based methods using fermentation of sugars using genetically modified microorganisms have been developed [84]. Several long chain fatty acids such as oleic acid, erucic acid, ricinoleic acid, vernolic acid, etc., can be synthesized from renewable resources such as plant oils.
and fats, which are considered as a good building blocks for the production of polyester and polyamide.

Among the wide range of monomers available from renewable resources, carboxylic acids such as succinic acid (SA) and itaconic acid (IA) have received much attention and produced interesting materials. Other worth mentioning but less-common carboxylic acids include, e.g., tartaric acid (TA) and citric acid (CA) [85, 86].

**Renewable Aromatic Monomers**

The aromatic polyesters are having very good properties like high molecular weights and higher melting and glass transition temperatures compared to aliphatic polyesters. The high performance thermoplastic polyethylene terephthalate and poly(butylene terephthalate) (PBT) are the main commercial examples of aromatic polyesters. But, the precursors used for the production of above fibres are fossil-based rather than renewable feedstock and hence are not degradable under normal environmental conditions. Hence, considerable research has been done in aromatic polyester fibre production to imitate their excellent properties using renewable monomers and to make them biodegradable [62]. For the production of aromatic monomers, lignin and carbohydrates are considered as the major sources, with 2,5-furandicarboxylic acid (FDCA) and vanillic acid as the significant examples to be emphasized.

Lignin is one of the main noncarbohydrate components in a lignocellulosic biomass, due to its distinctive chemical structures and properties, it offers wide range of possibilities for the production of several bio-based aromatic materials which are not possible through chemical or biological modifications of other biomass feed stocks. Vanillin is an aromatic aldehyde which is extracted from the genus *Vanilla planifolia*. At present, only vanillic acid is synthesized by means of oxidation of ligno-sulfonates. It is obtained by means of air oxidation of lignin in the presence of metal catalysts. It is also possible to produce vanillic acid by bio-based process using fungi, bacteria, or genetically modified microorganisms.

2,5-Furandicarboxylic acid (FDCA) is considered as the most capable monomer for the synthesis of bio-based polyester compared to chemical-based monomers. At present, FDCA is synthesized from biomass feed stocks, and it could be synthesized through bio-catalytic approach starting from HMF. Alternatively, enzymes could also be used for the bioconversion of HMF into FDCA [47, 87]. Other interesting bio-based furan monomers for polyester or polyamide synthesis include 2,5-bis(hydroxyl methyl)furan (BHMF), 2,5-bis(hydroxyl methyl)-tetrahydro furan, 2,5-bis(amino methyl)furan, and 2,5-bis(aminomethyl)tetrahydro furan [88].

**Conclusions and Recommendations for Going Forward**

Synthetic fibers have shown remarkable growth since 1950s, and they are raw materials for most clothings. But in recent years, increasing oil prices, reduction of oil feed stocks, growing awareness over environment, increasing greenhouse gases, and global warming have led to the development of materials from natural renewable
resources. In this aspect, bio-polymers provide significant positive impact on environment by reducing dependence of fossil fuels, reduced CO₂ emissions, etc. Large number of companies are involved in producing these bio-polymers. Also R&D works focusing on development of technologies to make biopolymers are contributing to its growth.

The processes which use renewable feed stocks are most promising one in the future for the development of biopolymer products. Biodegradable plastics comprising starch or cellulose fibers seems to be the most likely to have potential growth in usage. Time is of the essence for biodegradable polymer development, as society’s current views on environmental responsibility make this an ideal time for further growth of biopolymers. The challenges that should be take into consideration with reference to the production of bio-based polyesters and bio-plastics in the future are (i) the sustainable way of managing raw material resources, (ii) the sustainable production of chemicals as well as polymeric materials from bio-based materials, (iii) the performance of the bio-based materials in a long run, and (iv) economy of production and commercialization. To make these technologies economically viable, it is essential to develop logistics for biomass feed-stocks, novel production routes with high yields, new microbial enzymes, and effective downstream processing techniques for recovery of bio-based products. The current bio-based industry is focusing on production of bio-polymers from existing monomers and polymers.

Biodegradable plastics manufactured from microorganisms are future technology but economical feasibility of the same has to be taken into account. Apart from the economical point of view, the yield of the fermentation process is also very low in biotechnological route. Hence, enhancement in fermentation process is a major challenge for enlarging the range of monomers available at an industrial production like PLA. The commercialization of bio-based polymers is still in the early stages and expansion of bio-based polymers is also hindered mainly by economical aspects as the currently available bio-based chemicals and polymers are not economical compared to petroleum products. Hence, two methods look logical in the short-medium term to encourage the growth of bio-based products: (i) to produce bioversions of the existing fossil-based polymers as like Sorana®, a PTT from DuPont, which produced from renewable 1,3-propanediol and petrochemical TPA, and (ii) to gradually replacing petroleum based homologues with their renewable-based homologues, e.g., Avantium, which produces FDCA, has announced the development of the first PEF bottle.

In the near future, polymer chemistry could introduce bio-based monomers within existing productive processes and create promising building blocks for the production of monomers. In that respect, the possibility to tune polymer functional properties and biodegradability by means of optimized biocatalysts will guide the development of new effective polymers. Significant issues that are so far unresolved and which require further research are the development of an agreed methodology for the evaluation of emissions from direct and indirect land use change and the quantification of the impacts of biomass production on regional biodiversity. Such assessments should be complemented by further approaches like environmental risk assessment, or certification approaches for good and sustainable agricultural
practices like eco-management and audit schemes. Currently, no single approach gives a complete and balanced picture.

Bio-based polymers could replace the conventional polymers in near future. Currently, bio-based polymers are usually found in several applications from goods to hi-tech applications due to developments in biotechnologies and public awareness. Nevertheless, regardless of these developments, there are still some drawbacks which prevent the wider commercialization of bio-based polymers in many applications. This is mainly due to performance and price when compared with their conventional counterparts, which remains a significant challenge for bio-based polymers.

References

2. Gardetti MA, Torres AL (2013a) Sustainability in fashion and textiles: values, design, production and consumption. Greenleaf, UK