Biosynthetic Fibers: Production, Processing, Properties and Their Sustainability Parameters

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Abstract This chapter discusses the properties of some existing and newly developed biosynthetic fibers such as polylactic acid (PLA), soybean protein, casein, alginate, chitin, and chitosan. Production technologies of these fibers and their impact on various sustainability parameters are also discussed. Existing applications of these biosynthetic fibers are presented. The last section of this paper presents lifecycle assessment studies to assess the environmental impacts and sustainability aspects of PLA fibers.

Keywords Biosynthetic fibers · Production · Applications · Sustainability · Lifecycle assessment

1 Introduction

Biosynthetic fibers are defined as the manmade fibers synthesized from natural polymers. Among the various biosynthetic fibers, those produced from corn (polylactic acid or PLA), soybean (soybean protein fiber or SPF), milk (casein fiber), and seafood (chitin and chitosan) are becoming very popular due to their attractive properties and potential for diversified applications as well as environmental benefits. Among the various biosynthetic fibers, PLA is being produced currently on a

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S. S. Muthu (ed.), *Roadmap to Sustainable Textiles and Clothing*,
Textile Science and Clothing Technology, DOI: 10.1007/978-981-287-065-0_4,

large scale. PLA fibers are finding numerous applications in which petrochemical-based fibers are currently used. For example, PLA fiber can be used in bottle-making replacing PET fibers. Very important benefits of PLA over other petrochemical-based fibers are the renewable production source and biodegradability. Therefore, PLA, both in polymer and fiber forms, is considered to have less environmental impacts and more sustainability. In order to investigate the sustainability issues of PLA, lifecycle assessment (LCA) studies have been performed by various researchers on the PLA production process, and environmental impacts of PLA have been compared with other petrochemical-based polymers and fibers. Other biosynthetic fibers discussed in this chapter are mainly in the research stage and produced only on a small scale. However, they have been already considered as potential materials for many interesting applications and therefore, their sustainability aspects need to be investigated in the future. The following sections discuss the properties, production, and applications of major biosynthetic fibers produced to date. Also, LCA studies carried out on PLA have been discussed in detail.

2 Biosynthetic Fibers and Their Properties

2.1 Poly (Lactic Acid) Fiber

PLA is a linear aliphatic thermoplastic polyester derived from 100 % renewable sources such as corn, sugarcane, and sugar beet, and the polymer is biodegradable. A large-scale and economic production system of PLA for applications in fiber and packaging has been developed by NatureWorks LLC. The reasons behind widespread applications of PLA in the textile sector are its availability from annually renewable crops, 100 % degradability, and the possibility of reducing Earth's carbon dioxide level through its lifecycle. PLA fibers are considered as a totally novel class of synthetic fibers produced from annually renewable crops and are melt-spinnable [1–3].

2.1.1 PLA Fiber Properties

PLA fiber has many similar properties to common thermoplastic fibers, for example, a controlled crimp, smooth surface, and low moisture regain. One unique property of this fiber is that it is the only melt-processable fiber produced from annually renewable natural resources. Its mechanical properties are considered to be comparable to those of conventional polyester (PET) fiber, and probably due to its lower melting and softening temperatures, its comparison to polypropylene (PP) is also appropriate [4, 5]. The physical properties of PLA fiber are provided below.

- **Appearance:** Usually, PLA fibers have a circular cross-section and smooth surface.

- **Density:** PLA has a density of 1.25 g cm^{-3}, which is lower than natural fibers and PET.
- **Refractive index:** The refractive index of PLA fiber lies between 1.35–1.45.
- **Thermal properties:** PLA is a rigid fiber at room temperature. It shows glass transition temperature (T_g) between 55–65 °C and melting temperature (T_m) between 160–170 °C.
- **Crimp:** PLA can possess a good degree of crimp which is retained throughout fiber processing stages.
- **Tenacity:** Tenacity lies between 32–36 cN/tex, which is higher compared to natural fibers. Humidity cannot affect the strength of PLA at ambient temperature. However, higher temperature leads to significant deterioration of tenacity with concomitant increase in the fiber extensibility.
- **Moisture regain:** As compared to natural fibers, PLA possesses very low moisture regain (0.4–0.6 %), which is slightly higher than PET fiber.
- **Flammability:** Even upon removal of the heat source, PLA fiber burns for 2 min with white flame and low smoke generation. Higher LOI (limiting oxygen index) of PLA than many other textile fibers makes PLA very difficult to ignite due to the requirement of a higher oxygen level.
- **UV resistance:** PLA fiber shows much better resistance and insignificant strength loss due to exposure to UV light as compared to petroleum-based fibers.
- **Moisture transport:** PLA shows excellent moisture transport and wicking behavior.
- **Biological resistance:** PLA fibers cannot provide protection against microorganisms as inherently they don't have antimicrobial properties.
- **Chemical resistance:** Being a linear aliphatic fiber, it is prone to hydrolysis and chemical attack.
- **Solubility:** PLA has good resistance against dry-cleaning solvents.

2.2 Lactron Fiber

Lactron is the trade name of PLA fiber produced by Kanebo, Japan through fermentation of cornstarch.

2.2.1 Physical Properties of Lactron Fiber

Lactron fiber possesses a smooth appearance and silky luster, and has similar physical properties to conventional synthetic fibers such as nylon and polyester. Its strength and elongation can be altered by adjusting the production conditions [6]. The physical properties of Lactron fiber are presented in Table 1.

Table 1 Physical properties of lactron fiber and comparison with polyester fiber [6]

	Lactron fiber		Polyester fiber
	Multifilament	Monofilament	
Tensile strength (cN/dtex)	4.0–4.8	4.0–4.4	4.0–4.8
Elongation (%)	30–40	25–35	30–40
Young's modulus (kg/mm^2)	400–600	400–600	1100–1300
Crystallinity (%)	over 70	over 70	50–60
Melting point (°C)	175	175	265

2.3 Soybean Protein Fiber

Soybean protein fiber (SPF) is the only protein fiber derived from renewable and plant sources. A novel bioengineering technology is applied to produce this fiber from soybean cake. It is considered to be the healthy, comfortable, and green fiber of modern times. This fiber is produced from soybean protein which can be produced in massive quantities and at low cost. SPF possesses several attractive features that can meet the demands of comfortable, beautiful, and easy-care clothing [7–12].

2.3.1 Properties of SPF

Fabrics made from SPF have the following properties [9–15].

- **Magnificent and noble appearance:** SPF has a luster like silk fiber and an excellent draping ability making the fabric more attractive and elegant.
- **Outstanding comfort:** Along with excellent appearance, fabrics made from SPF are extremely comfortable due to excellent moisture absorption (similar to cotton) as well as moisture transmission characteristics (better than cotton).
- **Good physical property:** Single SPF has tenacity of more than 3.0 cN/dtex, which is higher than that of other natural fibers such as cotton, wool, and silk and only lower than PET fiber. Crease resistance, easy wash, and fast dry are the useful characteristics of SPF fabrics.
- Under a microscope, SPFs are translucent and present almost circular cross-section and smooth surface often containing some granulation and streakiness.
- The color of soybean fiber may be brownish, yellowish, white, or light tan. Similar to scoured wool, staple soybean fibers are loose, fluffy, soft to touch, and have good resiliency.
- Fabrics made from SPF are warm and comfortable due to high moisture absorption of SPF as well as its high heat of wetting. SPF has moisture regains of 16.1 and 12.9 % when it comes to equilibrium from wet and dry states, respectively.
- The strength of SPF is affected by humidity. Its wet strength is only 35–50 % of its dry strength.

2.4 Casein Fiber

Casein fiber technology provided the alternative way to enjoy some of the advantageous features of milk without actually drinking it but wearing in the form of fabrics. Casein fiber is produced from skimmed cow's milk and therefore, the main component of this fiber is the casein proteins containing 15 types of amino acids. These amino acids help in nourishment of the skin. Milk protein fiber is an outcome of nature, science, and technology and therefore, it possesses advantageous features of both natural and synthetic fibers. The fiber shows a glossy appearance similar to Mulberry silk. Casein fibers are capable of performing biological healthcare functions and exhibit natural and long-lasting antibacterial effects. The fabrics made from these fibers show excellent water transportation and air-permeability and therefore, are highly comfortable. The fabrics are light and soft. Casein fibers are resistant to fungus, insects, and aging. They show a pH similar to that of human skin. Biodegradability and renewability are other important features of these fibers. Casein fibers can be woven into light weaves with a lovely silky look that allows the skin to breathe and to absorb moisture [16, 17].

2.4.1 Properties of Casein Fiber

The fiber is white in color, lustrous, and its cross-section varies from bean to almost round shaped with a smooth surface and faint striations [16, 17].

2.4.2 Physical Properties of Casein Fiber

- **Tensile strength:** Casein fiber has a dry tenacity in the range of 8.0–9.7 cN/tex. When wet, it loses much of its strength and the tenacity falls in the range of 2.6–5.3 cN/tex.
- **Elongation:** 60–70 %, wet or dry.
- **Thermal properties:** The fibers generally soften on heating, particularly when wet. Fibers become brittle and yellow on prolonged heating.
- **Effect of moisture:** Casein fiber tends to absorb moisture readily and the fibers become swollen and soft.

2.4.3 Chemical Properties of Casein Fiber

- **Effect of Acids:** Casein fiber is stable to acids of moderate strength under normal conditions; it can be carbonized with cold 2 % sulfuric acid solution. Casein fiber disintegrates in strong mineral acids, and it resists dilute mineral acids and weak organic acids even at elevated temperatures. The fiber loses strength to a small extent and embrittlement may occur after boiling for long time.

- **Effect of Alkalis:** Casein fibers are sensitive to alkali. A mild alkali such as sodium bicarbonate and disodium hydrogen phosphate has an insignificant effect at low temperatures. Strong alkalis, such as caustic soda or soda ash cause severe swelling and ultimately disintegrate the fiber.
- **Effect of Organic Solvents:** Dry-cleaning solvents are not harmful to the casein fibers.
- **Insects:** Casein fiber is more resistant to attack by moth grubs as compared to wool. However, they may be damaged when blended with wool.
- **Micro-organisms:** Casein fibers are attacked by mildew, particularly in moist conditions.
- **Electrical Properties:** The dielectric strength of casein fibers is low.
- **Other Properties:** Casein fibers are similar to wool in the sense that they are naturally crimped and yarns have a characteristic warmth, softness, resiliency, and fullness of handling. Casein fibers provide good thermal insulation.

2.4.4 Comparison of Casein Fiber Properties with Other Natural Fibers

The physical properties of casein fiber are provided in Table 2 and compared with cotton, silk, and wool fibers.

2.5 Chitin and Chitosan Fiber

Chitin and chitosan fibers have been known for a long time. In the early stages of man-made fiber development, chitin was once recognized as a potential raw material for producing artificial silk. A number of attractive features were also observed in these fibers, such as their biocompatibility, biodegradability, non-toxicity, and in the case of chitosan, which is a polycationic polymer, the ability to form chelate with heavy metals. Wound-healing properties made these fibers appealing for sutures and wound dressings. Due to these interesting properties, extensive research has been conducted on chitin and chitosan fibers in recent years. The word “chitin” came from the Greek word *chiton* which means tunic or coat of mail, and this reveals the fact that chitin was first observed in the exoskeletons of fungi, shells, and bones. Chitin is found widely in cell walls of fungi, molds, and yeasts, and in the cuticular and exoskeletons of invertebrates, such as crabs, shrimps, and insects. Commercially, chitin is mainly produced from the wastes generated by the seafood industries such as shell wastes of crabs, shrimp, and krill. Chitosan is found only in a few species of fungi. Commercially, chitosan is produced from chitin through a deacetylation process using concentrated alkali solutions at elevated temperatures. The acetamide groups in chitin are hydrolyzed forming chitosan [18–25].

Table 2 Comparison of casein fiber properties with other natural fibers [17]

Property	Casein fiber	Cotton	Silk	Wool
Length (mm)	38	25–39	–	58–100
Fineness (dtex)	1.52	1.2–2.0	1.0–2.8	6–9
Dry tensile strength(cN/dtex)	2.8	1.9–3.1	3.8–4.0	2.6–3.5
Dry breaking elongation (%)	25–35	7–10	11–16	14–25
Wet tensile strength (cN/dtex)	2.4	3.2	2.1–2.8	0.8
Wet breaking elongation (%)	28.8	13	27–33	50
Frictional coefficient (static)	0.187	–	0.52	0.24
Frictional coefficient (dynamic)	0.214	–	0.26	0.384
Initial modulus (cN/dtex)	60–80	60–82	60–80	44–88
Moisture regain (%)	5–8	7–8	8–9	15–17
Density (g/cm^3)	1.22	1.50–1.54	1.46–1.52	1.34–1.38

Table 3 Comparison of properties of chitin and chitosan fibers with some typical commercial fibers [25]

Fiber	Fiber density (g/cm^3)	Moisture regain (%)	Tenacity (g/tex)	Extensibility (%)
Viscose	1.52	12–16	1.5–4.5	9–36
Cellulose acetate	1.30	6–6.5	1.0–1.26	23–45
Acrylic	1.17	1.5	1.8–4.5	16–50
Chitin	1.39	10–12.5	1.2–2.2	7–33
Chitosan	1.39	16.2	0.61–2.48	5.7–19.3

2.5.1 Properties of Chitin and Chitosan Fiber

The properties of chitin and chitosan fibers and some other commercial fibers are provided in Table 3. Chitin and chitosan fibers have similar mechanical properties to those of viscose rayon fibers. Typically, chitin fibers have tenacity of about 2 g/denier and extensibility of about 10 %. When chitosan fibers are acetylated to produce chitin fibers, fiber dry strength increases with the increasing degree of acetylation. The fiber wet strength shows an initial decrease but increases significantly upon further increase in the degree of acetylation. Chitin is a highly crystalline polymer inasmuch as the acetamide groups are capable of forming hydrogen bonding. The increase of both dry and wet strengths with an increase in the degree of acetylation is attributed to the interchain forces and increase in the degree of crystallinity. Chitin fibers possess a highly oriented structure when they are stretched, especially in the dry-jet wet-spinning process.

Chitin and chitosan fibers have thermal properties similar to those of cellulosic fibers. They do not melt but degradation occurs at elevated temperatures. In an inert atmosphere, chitosan fibers degrade at lower temperatures than chitin fibers. Both chitin and chitosan fibers possess a round cross-section under most spinning conditions [18, 19, 23–25]. Table 3 compares the properties of chitin and chitosan fibers with viscose, cellulose acetate, and acrylic fiber.

2.6 Alginate Fibers

Alginate is made up of a linear block copolymer of α-L-gularonic acid and β-D-mannuronic acid. However, the seaweed source as well as the growing conditions of the weed have a strong influence on the structure. Alginate-bearing weeds are typically found in low temperature or cold water. Major commercial sources of alginates are the giant kelp from California. The major manufacturers are situated near the weed sources in San Diego, Scotland, and Norway. More recently, manufacturers have been developing in Asia. Alginate can also be produced from a bacterial source.

Alginate in one form or another is used in the food industry, pharmaceuticals, and textiles. The most important source of commercial alginates is brown algae. Alginate is the main constituent of brown algae and is found in the cell wall and intercellular regions. However, only three types of brown algae are sufficiently abundant or suitable for commercial extraction of the alginic acid. In order of abundance, they are laminaria, microcystis, and ascophyllum. Laminariales are the largest algae and most complex. They are composed of a lamina (frond), a stipe (stem), and a basal (roots). Plants of laminaria vary in length with age, reaching a maximum of 3 m and because they present a large surface area to a turbulent environment, need to be firmly anchored to the substratum. Generally, marine algae are indifferent to the chemical composition of the substratum as they absorb minerals directly from the sea over their whole surface unlike surface plants, which absorb their nutrients from the soil. Harvesting is easy because most brown seaweeds grow in shallow water [24, 26–28].

2.6.1 Properties of Alginate Fiber

Calcium alginate can be stretched to achieve a high degree of orientation and high crystallinity [24, 26]. However, even after stretching, the degree of orientation and crystallinity of alginate fiber is lower as compared to other natural fibers. Alkali-resistant alginates (beryllium and chromium) have few ionic bonds but considerable coordinate links, which are more stable. These links decrease extensibility but increase tenacity of the fibers. There is a relationship between metal content and tensile strength and a 10 % metal content gives the highest fiber strength.

2.6.2 Physical Properties of Calcium Alginate Fiber

- Tenacity: 18.3 cN/tex. The tenacity in wet condition is significantly lower (<3 cN/tex).
- Extension at break: 14.0 %, which is sufficiently high to meet most textile requirements both in use and during processing.
- Density: 1.78 g/cm^3.

2.6.3 Thermal Properties of Alginic Acid Based Fibers

On heating below 50 °C highly polymerized alginic acid depolymerizes to give a stable low molecular weight alginic acid. Sodium alginate with a degree of polymerization of 500 can be stored for three years, without observable change, at temperatures between 10 and 20 °C. But at temperatures above 50 °C, degradation of high molecular weight sodium alginate can occur. The presence of moisture increases the rate of degradation.

2.6.4 Biodegradation of Alginate Fiber

Degradation of alginate may occur due to a variety of factors, which include light, water, atmospheric composition, fungi, and microorganisms. Moisture content plays an important role in the degradation process due to microorganisms and bacteria [24, 26].

3 Production Process of Biosynthetic Fibers

3.1 Production Process of PLA Fiber

PLA polymer can be produced either by direct condensation of lactic acid or via the cyclic intermediate dimer (lactide) through a ring-opening process (Fig. 1).

3.1.1 Polycondensation of Lactic Acid

In this process, water is removed due to the condensation reaction of lactic acid under high vacuum and temperature. This method results in the production of only low to intermediate-molecular–weight polymers due to the difficulties of removing water and impurities. Moreover, this method requires a relatively large reactor and has other disadvantages such as the need for evaporation, recovery of the solvent, and increased color and racemization [29, 30].

3.1.2 Ring-Opening Polymerization

The better way to produce high molecular weight PLA polymer is through ring-opening polymerization. This method has now been commercialized due to the low-cost production process of lactic acid through fermentation of corn dextrose which produces chiral lactic acid inexpensively in high yield. Lactic acid produced from the fermentation process contains 99.5 % of the L-isomer and 0.5 % of the

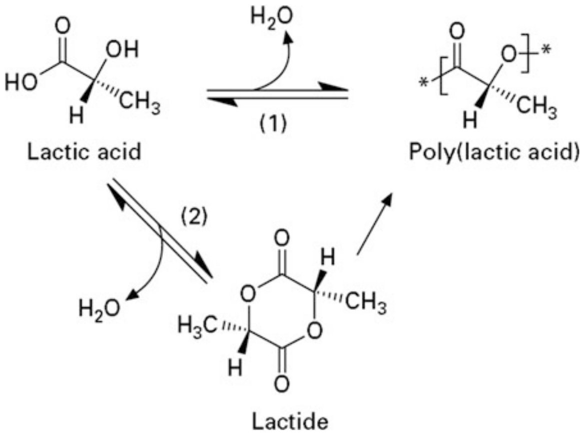

Fig. 1 Polymerization routes of PLA [29]

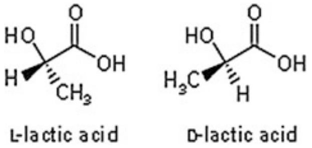

Fig. 2 Stereo isomers of lactic acid [29]

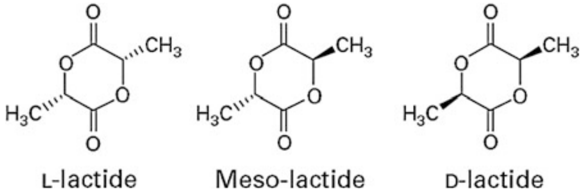

Fig. 3 Dimeric lactide isomers [29]

D-isomer unlike chemically synthesized lactic acid which gives the racemic mixture (50 % D and 50 % L; see Fig. 2).

In this process, a cyclic intermediate dimer, known as lactide, is produced as a result of water removal under milder conditions, without using solvent. This intermediate dimer is readily purified under vacuum distillation, and ring-opening polymerization is carried out using heat but without solvent. Cyclic lactide dimer is produced in three potential forms: D,D-lactide (called D-lactide), L,L-lactide(called L-lactide), and L,D- or D,L-lactide (called meso-lactide) (Fig. 3). Meso-lactide is not optically active whereas D and L-lactides are optically active. Before the ring-opening reaction, the lactide stream is divided into a low D-lactide stream and a high D/meso-lactide stream. Crystalline polymers can be obtained with high L-lactide levels, whereas a higher D-lactide level (>15 %) can lead to amorphous polymer. Polymers with a wide range of molecular weights can be produced by controlling the purity of the lactides, and polymer backbones containing different amount and sequence of D-lactide units result in differences in melt behavior, thermal properties, barrier properties, and ductility.

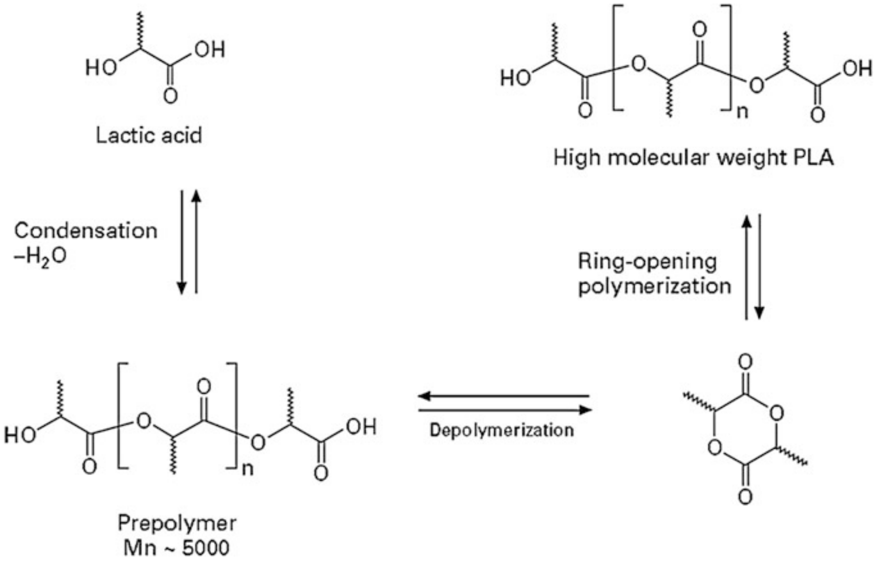

Fig. 4 Production of high molecular weight PLA via prepolymer and lactide formations [29]

Based on the concept of the lactide intermediate method, a low-cost and continuous production process of PLA has been patented by NatureWorks LLC. Instead of using solvent, this company developed the process of synthesizing both lactide and PLA in the melt, leading to substantial environmental and economic benefits. In this process, a low molecular weight PLA prepolymer is produced from the continuous condensation reaction of aqueous lactic acid (Fig. 4).

After the condensation reaction, conversion of the produced prepolymer into a mixture of lactide stereo isomers is carried out using tin catalyst in order to enhance the rate and selectivity of the intramolecular cyclization reaction. After purification of the molten lactide through vacuum distillation, a tin-catalyzed ring-opening polymerization of molten lactide is carried out to produce high molecular weight PLA polymer. The remaining monomers are then removed under vacuum and recycled back to the beginning of the process (Fig. 5) [29, 30].

3.1.3 Sustainability of PLA

As a fiber produced through melt spinning from a renewable source, this fiber presents numerous benefits over other synthetic as well as natural fibers. The sustainability aspects of PLA fibers are as follows [31].

- Similar to natural fibers, it is produced from renewable and nonpolluting raw materials and, therefore, it does not create problems associated with the use of oil-based raw materials.

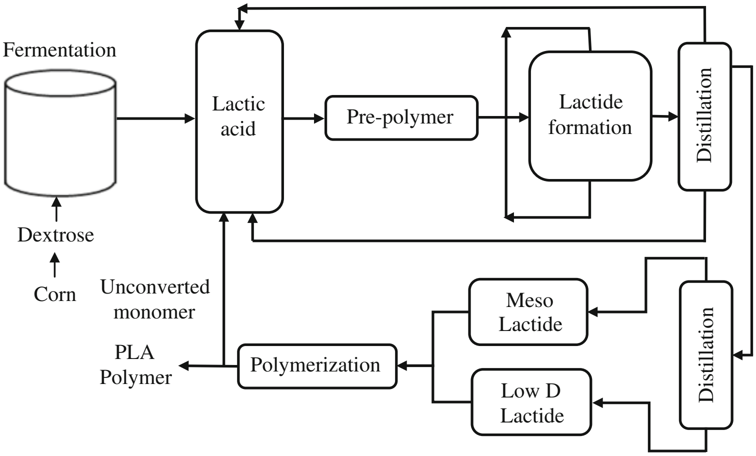

Fig. 5 Nonsolvent process to prepare polylactic acid [29]

- PLA is a biodegradable fiber, readily consumed by microbes at 98 % humidity and 60 °C or higher, and the decomposed materials can be used as fertilizers for the growth of more corn, beets, rice, and so on for future production of PLA. Therefore, PLA is more environmentally favorable compared to the non biodegradable synthetic polymers that can be recycled, because recycling can be done for only a limited number times until the polymers become useless [31].
- PLA is even more environmentally friendly than other biodegradable thermoplastics due to conversion of the entire mass of PLA into new PLA through natural processes, unlike many other biodegradable thermoplastics that use at least some materials obtained from the fossil fuels.
- However, there must be some use of energy in the PLA polymerization and subsequent production of fibers and fabrics and this can create a negative impact on the sustainability of PLA. The lifecycle of PLA is given in Fig. 6.

3.2 Production Process of Soybean Protein Fibers

The conversion of a globular protein into a fiber-forming protein is the primary requirement for producing soybean fibers and this is done through a cross-linking reaction. The main production stages of soybean fibers are as follows [9, 33, 34].

- **Separation**: “clarifying” the soya bean meal and precipitation of the protein.
- **Solubilization**: dissolution of resulting washed and dried protein into solvents to obtain the spinning solution.
- **Hardening**: forcing the spinning solution, when sufficiently ripened, through spinnerets into a coagulation bath resulting in fiber formation.

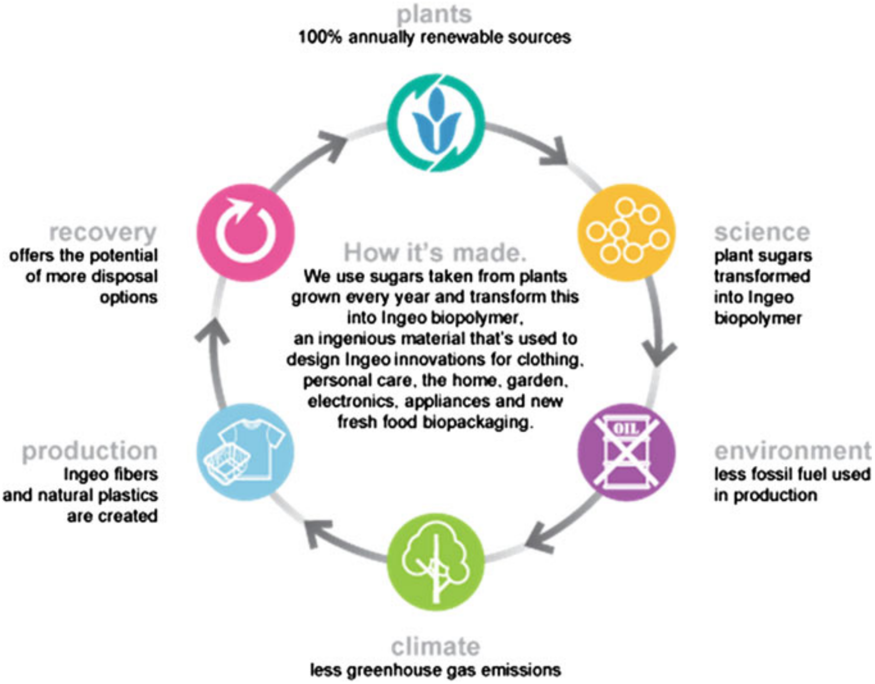

Fig. 6 PLA lifecycle [32]

- **Insolubilizing**: stretching and hardening, often using formaldehyde.
- **Controlled washing** and drying followed by cutting into staple fibers.

3.2.1 Production of Soybean Protein Curd

The extraction of suitable oil-free soybean protein is the most critical and also difficult step in the production of soybean fibers. The extraction of oil and other fatty substances from soybean flakes is commonly carried out by mechanical or solvent extraction. The extraction temperature has a strong influence on the degree of denaturation, and less soluble or darkened proteins are formed due to inappropriate temperatures. For production of fibers, lower temperature is used. The resulting oil-free substance is then dissolved in weak alkali solution with a pH ranging between 7 and 12. Oxidation can be prevented by adding reducing agents such as sodium sulphide or sodium sulphite (0.1 %). Next, clarification is performed by centrifuging or filtering and the protein is precipitated in the form of curd through the addition of acid. Excess acids and soluble salts are then removed from the protein by washing. A protein cake having a solid content of at least 60 % is prepared by draining the curd through filter cloth and then grated and dried at room temperature. Temperature and pH should be controlled properly in order to obtain a protein curd suitable for handling.

3.2.2 Preparation of Spinning Solution

A viscous solution, often called dope, is then prepared by again dissolving the soya protein. A high-viscosity spinning solution with high solid content up to 20 % is necessary to spin fibers. Difficulty arises during the spinning of fibers due to the tendency of soya protein to form gel at high concentrations. Partial hydrolysis of soya protein is then carried out using pepsin. Alternatively, alkali is used for complete hydrolysis. Subsequently, ageing or ripening of the protein solution is carried out to obtain the required high viscosity and stringiness. This process consists of mainly two stages: namely degradation in which breakage of peptide bonds occurs and denaturation in which molecules change their conformations from the original folded and globular state to random conformations. One important issue in this process is to control the enzymes and bacteria present in the solution.

3.2.3 Extrusion and Insolubilization of Fibers

After obtaining the required solution viscosity, wet spinning of SPF filaments is carried out by extruding the spinning dope through spinneret holes into a coagulation bath. After this, filaments are insolubilized (this process is also called tanning or hardening) by passing the coagulated filaments through a formaldehyde bath under acid conditions. This results in the formation of bonds between formaldehyde and lysine side-chain amino acids. Also, a secondary condensation reaction leads to formation of bonds between cyclic methylene complexes and other side-chain amino groups. Due to formation of these bonds and a complex network between the protein chains results in significant improvement in the wet strength of the fibers. To improve the flow characteristics of this solution, protein solvents such as formic, acetic, or lactic acids are added to the bath. Additionally, to reduce the stickiness of the newly formed fibers, formaldehyde, synthetic tanning agents, or other spinning aids, such as cation-active agents or anion-active soaps, can also be added [9, 33, 34].

3.3 Production Process of Casein fiber

The production steps of casein fibers are as follows [16, 17].

3.3.1 Raw Material (Casein)

Acid treatment of skimmed milk produces casein which coagulates as a curd. It is then washed, dried, and ground to a fine powder. To obtain 1 kg of casein, 35 l of skimmed milk are required.

3.3.2 Mixing, Filtration, and Deaeration

Blending of casein is carried out to minimize the effect of variations in quality. It is then dissolved in caustic soda and allowed to ripen and reach a viscosity suitable for the spinning process. Before spinning, the solution is filtered and deaerated.

3.3.3 Spinning

Casein fiber is produced through the wet spinning technique. The spinning dope is extruded through the spinneret into a coagulation bath composed of 2 parts sulfuric acid, 5 parts formaldehyde, 20 parts glucose and 100 parts water. After coagulation, casein filaments are formed and stretched to some degree. However, the spinning process cannot ensure good orientation of molecular chains and the crystal structure formation, and as a result, the as-spun fibers are soft, weak, and difficult to handle. Casein filaments soften and swell upon penetration of water which pushes apart the long casein molecules. The untreated casein fibers are not suitable for practical textile applications due to the adverse effect of water on this fiber. Therefore, these fibers are chemically modified to form cross-links between the adjacent molecules, in order to improve their strength and dimensional stability under wet conditions.

3.3.4 Cutting

After spinning, staple fibers are produced through a cutting process. This is necessary as the long filaments do not have sufficient strength to withstand further processes.

3.3.5 Hardening

To improve the water resistance of casein fiber, several techniques based on formaldehyde treatment have been developed and successfully used in practice.

3.3.6 Washing, Drying and Baling

After hardening, the fibers are washed, dried, and sent for the baling process.

3.4 Production Process of Chitin and Chitosan Fiber

Chitin and chitosan fibers cannot be melt-spun because their melting points are well above their degradation temperatures due to strong interchain bondings.

Therefore, these fibers are mostly produced through wet-spinning technology in which the polymers are first dissolved into a solvent, followed by extrusion and coagulation in a non solvent bath. Precipitation of the polymer in the coagulation bath leads to formation of filaments which are then washed, drawn, and dried [19, 20, 23–25].

3.4.1 Solvents for Chitins

One of the major challenges in spinning chitin fiber was to discover a suitable solvent for this polymer. The difficulty in dissolving chitin in solvents arises from its relatively inert chemical structure and semicrystalline physical structure. In 1936, a “syrupy colloidal solution” of chitin was prepared with aqueous lithium thio-cyanate solution saturated at about 60 °C and heated to 95 °C. Another process of dissolving chitin was developed based on chitin xanthate formation. In this process, chitin was steeped in a concentrated NaOH solution at room temperature and pressed to produce alkali chitin cake which was then shredded and shaken in a closed vessel with carbon disulfide. This mixture was stored for a long period and then mixed with crushed ice in a thermos jug. The chitin solution was prepared upon further mixing and storage. Chitin has also been dissolved effectively in solvents containing di- or tri-chloroaceticacid alone or in combination with organic solvents including formic acid, acetic acid, chloral hydrate, methylene chloride, and so on. Chitin fibers were also spun using a solution containing 40 % trichloroacetic acid, 40 % chloral hydrate, and 20 % methylene chloride. Hexafluoroisopropyl alcohol and hexafluoroacetone sesquihydrate are other chitin solvents that are used. Typically, 3 parts by weight of chitin can be dissolved in 97 parts of hexafluoroisopropyl alcohol through gentle stirring at 55 °C. All these solvent systems used for dissolving chitin are acid-based and some of them are either very corrosive or expensive. An important breakthrough in chitin spinning was the discovery of aprotic solvent systems such as dimethyl acetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) or mixtures of these amides with LiCl. These solvent systems do not lead to hydrolysis of chitin and the dissolution process can be greatly improved after pretreatment of chitin with *p*-toluenesulfonic acid in *i*-propanol.

3.4.2 Spinning of Fiber

Chitin is spun into filaments through a wet-spinning process using a DMAc–LiCl solvent system. Pretreatment with *p*-toluene sulfonic acid in *i*-propanol leads to decrease of chitin molecular weight from 23,106 to 1,53105 and facilitates its dissolution in DMAc–LiCl. A chitin solution containing about 5–9 % by weight of chitin is extruded through fine holes (diameter: 50–150 mm) into the coagulation bath or alternatively, extruded via spinnerets with relatively large diameters (150–400 mm) into an air gap before the filament is coagulated in a nonsolvent bath (dry-jet wet-spinning). A 75/25 mixture of DMAc and H_2O at temperatures between 40 and 75 °C or methanol at room temperature has been found to be the most effective coagulation bath composition.

3.4.3 Production of Chitosan Fiber

The first attempt at producing chitosan fibers was reported in 1980. A concentrated solution of 3 % chitosan dissolved in 0.5 % aqueous acetic acid was extruded into a 5 % aqueous NaOH bath and the produced fibers exhibited a tenacity of 2.44 g/denier, elongation at break of 10.8 %, and knot strength of 1.75 g/denier. In another process, 3 % chitosan dope in 1 % aqueous acetic acid was extruded into an aqueous bath containing 2 % Na lauryl sulfate. Use of di-chloro-acetic acid as the solvent and $CuCO_3$–NH_4OH as the coagulant was also tried. In another study, chitosan fiber was wet-spun using a urea–acetic acid mixture as the solvent and a coagulation bath containing 5 % aqueous NaOH and alcohol at ratio of 90:10. The produced fiber of 3.2 denier exhibited strength of 12.2 g with an extensibility of 17.2 %. Chitosan fibers using dopes in 2–4 % aqueous acetic acid and a coagulation bath containing $CuSO_4$–NH_4OH or $CuSO_4$–H_2SO_4 are also produced. The fibers produced using this process were a complex of chitosan and copper which was removed later on. In another study, a chitosan solution in 2 % aqueous acetic acid was extruded and coagulated in a dilute alkali solution to produce the chitosan filaments. Spinning variables such as jet stretch ratio, draw ratio, and coagulation bath composition were found to have very little effect on the fiber properties, whereas drying conditions showed a strong influence. Fibers with much higher extensibility were obtained using air drying as compared to radiant heating. A coagulation bath composition containing concentrated Na_2SO_4 with a small amount of NaOH resulted in the production of strong fibers [19, 20, 23–25].

3.5 Production of Alginate Fibers

The production process of alginate fibers consists of the following steps. First, seaweed is collected, dried, and milled and the powder is treated with aqueous sodium carbonate and sodium hydroxide to convert the alginate present in the seaweed powder into the sodium salt. Sodium carbonate treatment, however, does not dissolve pigments and cellulose present in the seaweed. Purification of sodium alginate is carried out through sedimentation of the produced viscous solution and subsequently, bleaching and sterilization are performed using sodium hypochlorite. Precipitation of alginic acid is then carried out through acidification and after washing, alginic acid is reconverted into pure sodium alginate, which is dried and milled to make powder.

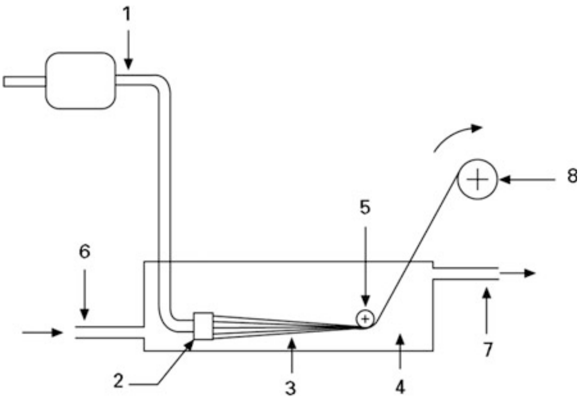

Fig. 7 Schematic diagram of a horizontal wet-spinning system. *1* Inlet of the spinning dope; *2* Spinneret; *3* Spinning line; *4* Coagulation bath; *5* Take-up godet; *6* and *7*. Inlet and outlet of the spinning bath [26]

Alginate fibers are produced using the wet-spinning method. A schematic diagram of alginate fiber spinning is provided in Fig. 7. A dilute solution of sodium alginate is prepared, filtered, spun, and passed through a coagulation bath containing certain polyvalent cation salts (Ca++, Al+++, etc.) or inorganic acid solution (0.02 N hydrochloric acid, emulsified oil, and a small amount of cationic surfactant). In the coagulation bath, sodium alginate is precipitated as a metal salt of alginic acid (e.g., calcium alginate) or alginic acid and drawn in the form of filaments, washed, lubricated, dried, and wound onto bobbins. The filaments can also be cut into staple fibers of the required length suitable for nonwoven products. The chemical reactions that occur in the coagulation process are presented in Fig. 8.

The composition and conditions of the coagulation bath strongly influence the morphological structure and properties of alginate fibers. In the production of typical calcium alginate fibers, a 6.4 % by weight of aqueous sodium alginate solution is extruded through a jet containing 20 holes into a bath containing 5 % salt of calcium chloride, 0.2 % acetic acid, and 0.05 % cetylpyridinium chloride (cation active compound) at 40 °C. Subsequently, the filaments are stretched by 37 % by passing them over godets, reeled into skeins, washed in a 0.1 % solution of calcium chloride at 80 °C, and then dried at room temperature [24, 26–28].

4 Applications of Biosynthetic Fibers

4.1 Application of PLA Fibers

PLA fibers can be used in wide range of woven, knitted, and nonwoven applications including: [6, 35]

- Clothing (fashion wear, underwear, sportswear, uniforms, etc.)
- Can be blended with wool, cotton, and silk fibers

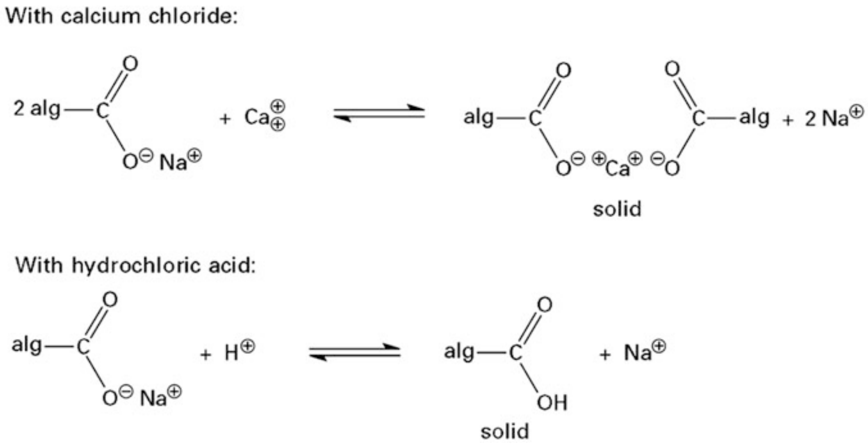

Fig. 8 Chemical reactions in coagulation process [26]

- Wipers
- Carpet tiles
- Diapers
- Feminine hygiene
- Upholstery
- Interior and outdoor furnishings
- Filtration
- Agricultural applications (Geotextiles for soil erosion control)
- Packaging.

4.2 Applications of Soybean Fibers

4.2.1 Yarn

Spinning methods for processing pure soybean fiber, its blends with natural (cotton, linen, wool, cashmere, and silk) and manmade fibers (modified polyester, viscose, tencel, polynosic, etc.) have been already established in the plants dealing with cotton, silk, and wool. One hundred percent soybean fiber yarns are produced in the liner density range of 21^S–80^S and blended yarns with linear density of 28/72, 30/70, 45/55, 60/40, 70/30, 85/15, and so on are possible. [8, 11, 12]

4.2.2 Knit Fabric

A superior soft hand along with moisture absorbency and permeability make soybean fiber suitable for application in high-grade knits and innerwear. These products are also given antibacterial and healthcare finishes to improve their functionalities.

4.2.3 Woven Fabric

Shirting and home textiles are the area where soybean fiber blends have far been used. Luster and soft hand, similar to silk, are the special features of these materials. Softness and smooth appearance as well as absorbency make soybean fiber products ideal for the cloths that are worn close to the skin such as underwear, sleepwear, sportswear, children's clothes, bed sheets, towels, and blankets.

4.2.4 Undergarments

Undergarments produced from SPF have excellent softness and comfort characteristics. Very pleasing breathability, easy stretch, and fine caring or a skin-on-skin feeling are the attractive features of SPF fabrics.

4.2.5 Baby Wear

Eco-friendly soybean baby clothing offers several benefits such as outstanding breathability, warmth, and comfort.

4.2.6 Skirts

SPF fabrics made of high-count yarns are fine and possess a clear appearance, excellent luster and drapability, and, therefore, are attractive for application in top-level skirts.

4.3 Applications of Casein Fiber

Casein fiber is used for intimate garments and is suitable for children's clothing because this fiber has bacteriostatic characteristics [16, 17]. As milk proteins are the main ingredient of casein fiber, it contains a natural humectants factor that can help lubricate and smoothen skin and maintain skin moisture reducing wrinkles.

Major usages of casein fibers are:

- Intimate garments
- Children's garments
- T-shirts
- Sweaters
- Women's garments
- Sports wear
- Uniforms
- Eye masks
- Bedding.

4.4 Applications of Chitin and Chitosan Fibers

Chitin and chitosan fibers find potential application in absorbable sutures and wound-dressing materials due to their ability to accelerate the wound healing. Chitin sutures are resistant to bile, urine, and pancreatic juice, which may degrade other absorbable sutures. Also, chitin and chitosan are also used in wastewater treatment as the heavy metal ions can be removed through chelation. Photography is another application area of chitosan due to its resistance to abrasion, its optical characteristics, and film-forming ability. Silver complexes can easily diffuse from one layer to another of a film because they are not significantly retained by chitosan. In the cosmetic industry, chitosan and its derivatives find wide applications in creams, lotions, nail lacquers, and the like.

4.4.1 Textile Applications of Chitin/Chitosan Fibers

- Sports: Uniforms of professional baseball players, wrist bands, underwear, slide pants, T-shirts, socks, sweat shirts, tennis socks, sweat bands, inside cloth of shoes [18–20, 22, 25, 36]
- Underwear: Infant, children, men, and women
- Pajamas
- Ladies wear
- Baby clothes: Outerwear and blankets
- House interior
- Beddings: Ticking, bed cover, and pillow case
- Towels
- Nonwoven fabric: Dish towels and mask filters.

4.5 Applications of Alginate Fiber

- Bandages [26, 27, 37]
- Adhesive strips
- Pads of various kinds
- Surgical sponges
- Tampons
- Theater curtains
- Wound dressings (nonwoven alginate fabric) and so on.

4.6 Sustainable Studies on PLA

Sustainability of PLA fibers has been studied through determination of their environmental impacts using lifecycle assessment (LCA). In one of these studies, LCA has been performed on PLA fibers produced by Cargill Dow. Two types of PLA production process were considered in this study, namely (1) the current production process (PLA1) and (2) the next-generation PLA production process based on biomass and wind power (PLA B/WP). This process differs from PLA1 process in that this process will use crop residue such as stems, straw, husks, leaves, and the like from corn or other crops as the primary feedstock instead of corn-derived dextrose. Fermentation sugar will be produced from cellulose and hemicellulose in a biorefinery and thermal energy will be generated from the combustion of the remaining lignin-rich materials for use in various conversion processes. In addition, wind power will be used for producing electricity. The flow diagrams of PLA1 and PLA B/WP processes are provided in Figs. 9 and 10. In the LCA analysis, the following stages of PLA production were considered: (a) corn growing, (b) transport of corn to the corn wet mill, (c) processing of corn into dextrose, (d) conversion of dextrose into lactic acid, (e) conversion of lactic acid into lactide, and (f) polymerization of lactide into polylactide pellets. The data source used for the LCA study was the SRI study on the lifecycle of polylactide [39]. The environmental impacts of PLA fiber were also compared with other conventional petrochemical polymers based on the data provided by the Association of Plastics Manufacturers in Europe (APME).

4.6.1 Contributions to the Gross Energy Requirement for PLA1 Process

Different contributions to the gross energy requirement (GER) for PLA1 process is presented in Fig. 11. The GER for PLA1 is 82.5 MJ/kg which is used in different stages of PLA production starting from corn growing to the ready-to-ship pellets. It can be noticed that the major part of energy use is the renewable energy representing the corn feedstock (15.5 % moisture), which can be only decreased by using less corn. The gross fossil energy use (GFEU), which is GER less the renewable energy embodied in the corn feedstock, is 54.1 MJ/kg of PLA. GFEU is an important indicator for the use of fossil energy in the form of coal, oil, gas, and nuclear energy and also for the translocation of carbon from the earth into the atmosphere along with other associated emissions such as sulfur oxides, hydrocarbons, and heavy metals [38].

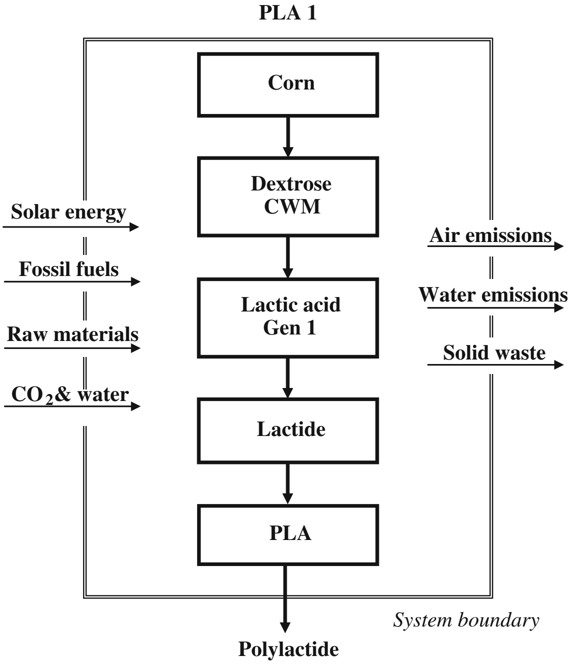

Fig. 9 System boundary for PLA1 process [38]

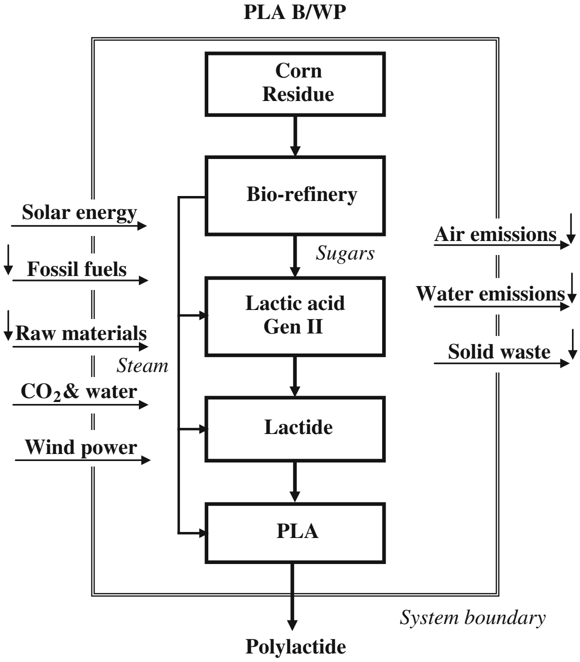

Fig. 10 Systems boundary for PLA production with biomass feedstock and wind energy input [38]

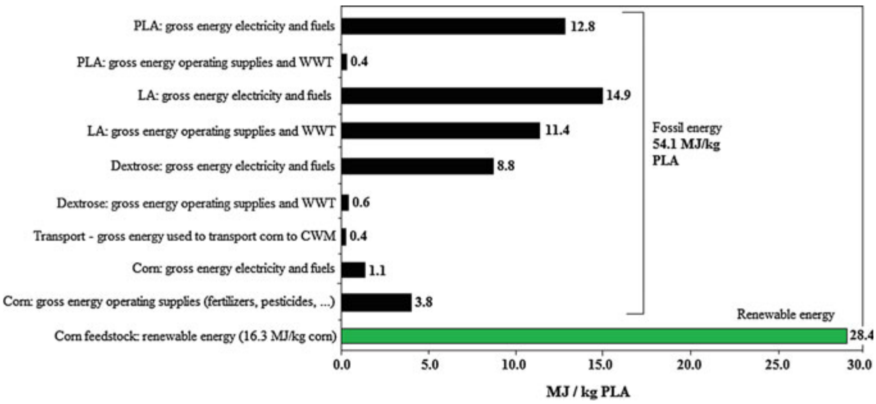

Fig. 11 Contributions to the gross energy requirement for PLA1 process [38]

4.6.2 Fossil Energy Use

The fossil energy use of PLA and other petrochemical polymers is presented in Fig. 12. From this analysis it is evident that fossil energy use is significantly lower in the case of PLA fibers as compared to other petrochemical-based polymers; the PLA1 process uses 25–55 % less energy whereas in case of the PLA process based on biomass and wind power (i.e., PLA B/WP) the fossil energy requirement is reduced more than 90 %. Therefore, PLA fibers present significant environmental benefits in terms of fossil energy as compared to the other petrochemical-based polymers [40].

4.6.3 Global Climate Change

The greenhouse gas emissions, which are responsible for global climate change, for PLA fibers and other petrochemical-based polymers are presented in Fig. 13. The global warming potential of the three largest greenhouse gases, namely carbon dioxide, methane, and dinitrogen oxide, was studied for a 100-year time horizon. CO_2 equivalents were calculated for the other two emissions and presented in the graph [41].

It can be seen from this comparison that PLA1 process is better than most of the polymers studied in terms of greenhouse gas emissions. Some polymers such as LDPE and PP give similar greenhouse gas emissions to PLA1 polymer. However, the most exciting finding is that the improved process of PLA production based on the use of crop residue as the feedstock and utilization of the lignin fraction of lingo-cellulosic feedstocks for process heat generation as well as wind power for electricity generation provide a negative greenhouse gas effect. Therefore, this improved process of PLA production can be used by manufacturing companies as a strategy to reduce greenhouse gas emissions [38].

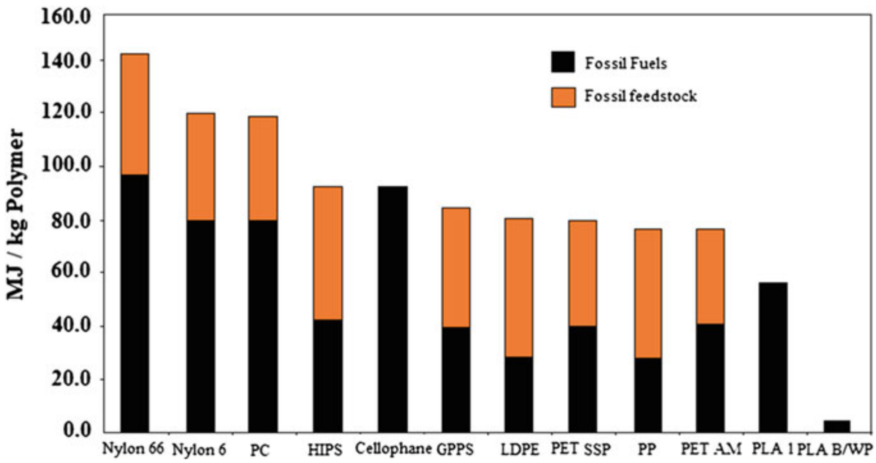

Fig. 12 Fossil energy requirement for some petroleum-based polymers and PLA. The cross-hashed part of the bars represents the fossil energy used as chemical feedstock (the fossil resource to build the polymer chain). The solid part of each bar represents the gross fossil energy use for the fuels and operations supplies used to drive the production processes. PC = polycarbonate; HIPS = high impact polystyrene; GPPS = general-purpose polystyrene; LDPE = low-density polyethylene; PET SSP = polyethylene terephthalate, solid-state polymerization (bottle grade); PP = polypropylene; PET AM = polyethylene terephthalate, amorphous (fibers and film grade); PLA1 = polylactide (first generation); PLA B/WP (polylactide, biomass/wind power scenario) [38]

4.6.4 Water Use

The results of water use, which is the sum of public supply, river, canal, sea, and well water for use as cooling water, process water, and irrigation water, of PLA and other petrochemical based polymers, are provided in Fig. 14. Although the PLA production process contains different stages that use water such as irrigation water during corn growing and the production of dextrose and lactic acid, the total amount of water required is significantly less compared to most of the studied polymers and comparable with some of the best-performing petrochemical polymers [38].

Better sustainability of PLA as compared to other petrochemical polymers has also been observed by other researchers. Groot et al. [42] performed an LCA study on PLLA (poly-L-lactic acid) produced from cane sugar in Thailand, and also compared the results with some petrochemical-based polymers. Figure 15 shows the global warming potential of these polymers. It can be observed that PLLA shows much lower GWP as compared to fossil-based polymers. The sequestration of CO_2 from the atmosphere and fixation into the polymers is the primary reason for the lower GWP of PLLA.

The primary energy demand for PLLA and other polymers is presented in Fig. 16. It can be seen that the gross energy demand (sum of renewable and nonrenewable energy) is at the same level for both PLLA and other petrochemical-

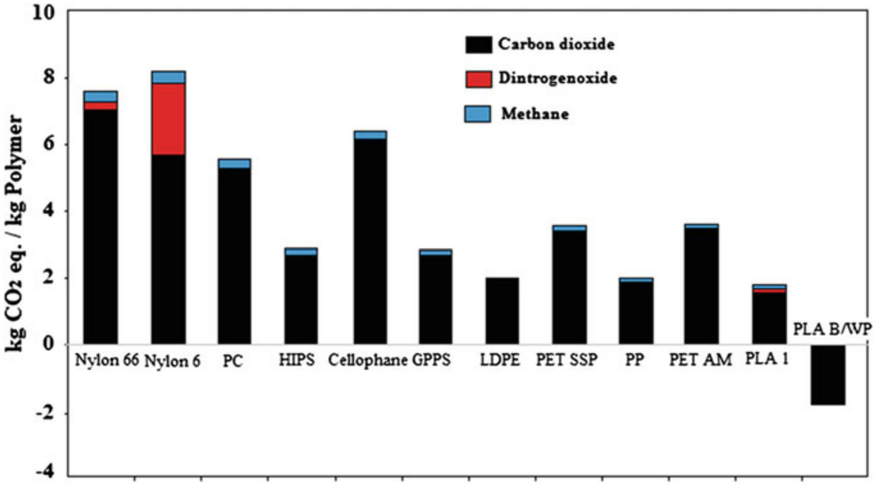

Fig. 13 Contributions to global climate change for some petrochemical polymers and PLA [38]

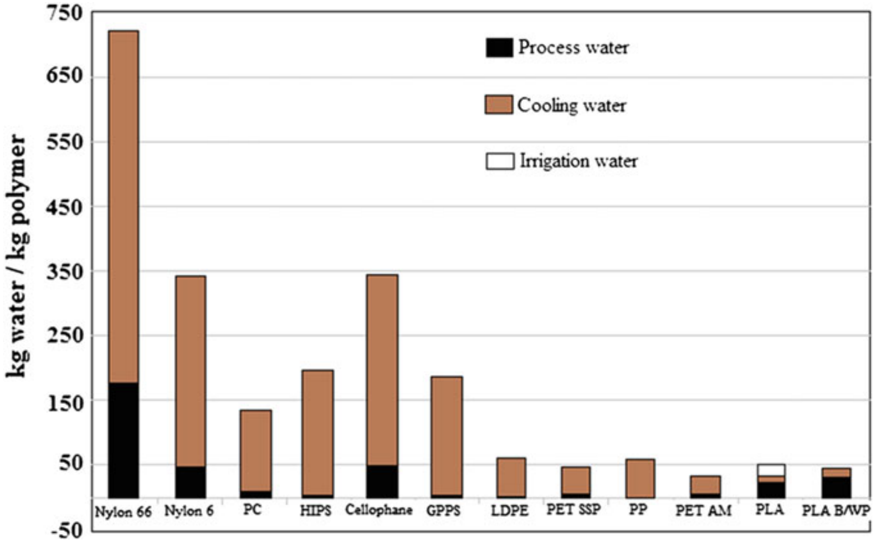

Fig. 14 Gross water use by petrochemical polymers and the two PLA cases [38]

based polymers. However, the production of PLLA is always beneficial inasmuch as a large part of the total energy is supplied by solar energy and this is used for fixation of CO_2 in the sugarcane plant.

From Fig. 17 which provides the normalized data for all impact categories, it can be commented that important impact categories for PLLA are eutrophication, acidification, and photochemical ozone creation. These environmental impacts are

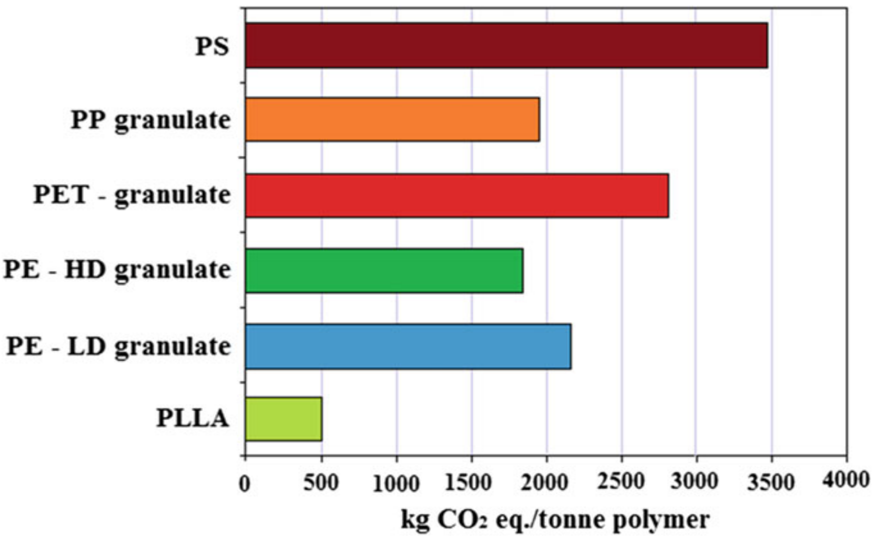

Fig. 15 GWP involved with the production of PLLA and other polymers

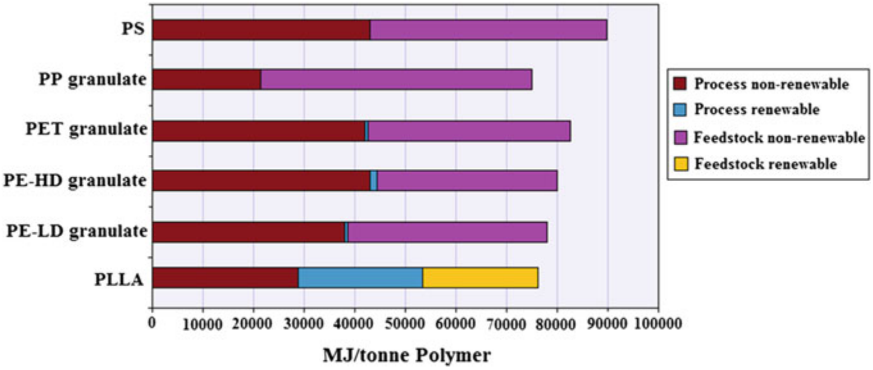

Fig. 16 Primary energy demand involved in the production of PLLA and other polymers

attributed to (a) N-leakage and NH_3 volatilization from an ammonia-based fertilizer in the soil, (b) NOx, SOx, and CO from cane trash burning in the field, and (c) uncontrolled NOx and SOx emissions in cane cultivation. The reduction of these factors is possible through detailed knowledge about the agricultural practices and use of emerging green economics and modern agricultural technologies.

In another LCA study carried out by Shen et al. [43], NREU and GHG emissions of PLA and other biobased and petrochemical polymers were analyzed and compared using LCA. It was observed that PLA fiber consumed lower NREU as compared to petrochemical and biobased PET and higher NREU than recycled polymers such as PET and biobased PET and regenerated cellulosic fibers.

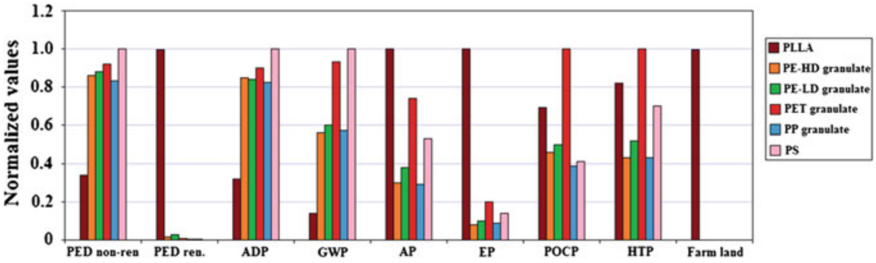

Fig. 17 Comparison of the most relevant ecological factors involved in the production of PLLA and fossil-based derived polymers

Similarly, the GHG emissions of PLA were lower than petrochemical and biobased PET and higher compared to recycled petrochemical and biobased PET, and regenerated cellulosic fibers.

5 Conclusions

This paper discussed the production, properties, and applications of PLA and other biosynthetic fibers. Also the sustainability aspects of PLA have been discussed in detail and compared with some commonly used petrochemical polymers. Biosynthetic fibers such as PLA, soybean, lactron, casein, chitin, and chitosan fibers present a wide range of properties making them suitable for diversified applications. Soybean protein fiber provides excellent softness, breathability, absorbency, comfort, and silk like appearance and is suitable for applications in underwear, sleepwear, baby clothing, and so on. The fiber derived from milk protein (i.e., casein fiber) also has silky appearance and bacteriostatic properties, making this fiber suitable for intimate wear and childreńs clothing. Chitin and chitosan fibers are based on raw materials obtained from the wastes generated by the seafood industries such as shell wastes of crabs, shrimp, and krill. These fibers are biodegradable, biocompatible, nontoxic, and exhibit antimicrobial properties, and due to these properties, they find widespread applications in suture and wound dressing. Among the various biosynthetic fibers, PLA has been widely studied due to its many advantageous features and similar properties to petroleum-based synthetic fibers. PLA can be produced through the spinning of polymers derived from renewable natural resources (corn) and it is completely biodegradable and causes much lower environmental impacts as compared to synthetic fibers and several natural fibers. It has been observed that the use of fossil energy, greenhouse gas emissions, and water use, which are the important factors influencing sustainability, are significantly lower in the case of PLA compared to most conventional synthetic polymers. Moreover, the improved process of PLA production based on the use of crop residue as the feedstock and utilization of the lignin fraction of lignocellulosic feedstocks for process heat generation as well as wind power for electricity generation provides significant environmental benefits over the conventional process and is, therefore, more sustainable.

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