Textile Science and Clothing Technology

Subramanian Senthilkannan Muthu *Editor*

Roadmap to Sustainable Textiles and Clothing

Eco-friendly Raw Materials, Technologies, and Processing Methods

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Preface

The concept of sustainability is widely used in every industrial sector, including textiles and clothing industry and is one of the important agendas of today's textiles and clothing sector. The textile and clothing sector consists of a fairly long supply chain, starting with fiber formation and ending at the apparel production and consisting of many intermittent stages. When it comes to the lifecycle of textile products, this entire lengthy supply chain occupies nearly half and the rest is left to the consumers in terms of use and disposal stages. Measuring and practicing the sustainability of textile products through this lengthy supply chain and across all the lifecycle phases of a textile product is not an easy task, but doable though.

Since its first definition, sustainability has been used and defined in different sectors in various forms and it has many faces and facets. Referring to the very first definition of sustainable development, stemming from the Brundtland Report, a sustainable textile product is the one that is created, produced, transported, used, and disposed of with the due consideration to environmental impacts, social aspects, and economic implications, thereby satisfying all three pillars of sustainability. In the entire life span and across all the lifecycle phases, a sustainable textile product is expected to create the minimum possible or very least environmental and social impacts.

Any product demands deployment of various resources throughout its entire lifecycle and textile products are no exception to this. In a typical lifecycle model, textile products need various material, energy, and process inputs and create various outputs in their stages from cradle to grave. In the case of sustainable textile products, all these inputs and outputs are expected to ensure environmental and social friendliness and safety to human health throughout the entire lifecycle phases, apart from utilizing renewable and/or recycled input streams. A sustainable textile product should begin and end its lifecycle as smoothly as possible without harming the environment and human beings.

The textiles and clothing supply chain employs a wide array of raw materials, auxiliaries, and a long list of processing methods/sequences. Lifecycle assessment study of textile materials consists of a fairly long inventory list, even for a very simple textile product without many accessories (say, even a simple cotton t-shirt). Embracing the concept of sustainable development for a clothing product is quite ambitious and a cumbersome process too, because this has to be implemented in the lengthy supply chain and across the various lifecycle phases. This is the main motivation of this roadmap series on sustainable textiles and clothing. In different volumes, this series covers detailed and minute aspects of sustainability in the textiles and clothing sector.

Volume one is the first step in this roadmap series and discusses sustainable (eco-friendly) raw materials, technologies, and processing methods in the textile and clothing sector. Information on sustainable raw materials and processing methods for the development of suitable textiles and clothing products is disseminated in this volume in 10 informative chapters dealing with various pertinent issues.

"Natural Plant Fibers: Production, Processing, Properties and Their Sustainability Parameters" deals with the topic of natural plant fibers. Among various natural plant fibers, very important fibers namely cotton, flax, jute, and hemp are chosen for discussion. This chapter includes various topics pertaining to these chosen fibers such as the present scenario, market trends, production, processing, and applications. And very importantly, this chapter highlights the details of various factors influencing the sustainability of these natural plant fibers by concentrating on various Lifecycle Assessment studies (LCA) on these fibers.

"Natural Dyes: Sources, Chemistry, Application and Sustainability Issues" and "Sustainable Dyeing with Synthetic Dyes" are dedicated to natural and synthetic dyes for textile application. "Natural Dyes: Sources, Chemistry, Application and Sustainability Issues" takes the readers through a complete journey on natural dyes covering the different sources, chemistry, and extraction of natural dyes, application methods, and various sustainability parameters and issues associated with the current natural dyes. With the similar frame, "Sustainable Dyeing with Synthetic Dyes" presents detailed discussions pertaining to the sustainability aspects of synthetic dyes. "Sustainable Dyeing with Synthetic Dyes" includes detailed discussions on the history of textile dyeing with synthetic dyes, an overview of synthetic dyes, and their applications on various textile materials by highlighting their sustainability aspects.

"Biosynthetic Fibers: Production, Processing, Properties and Their Sustainability Parameters" deals with the production, processing, applications, and sustainability implications of biosynthetic fibers. Potential fibers of this type, namely PLA (Poly Lactic Acid), soybean protein, casein, alginate, chitin, and chitosan are chosen for discussion in this chapter. LCA studies conducted on PLA fibers are also discussed to a great extent.

Another important topic under the captioned title of this volume of roadmap is recycling and applications of recycled fibers. "Textiles and Apparel Development Using Recycled and Reclaimed Fibers" is dedicated to the discussion of this important subject and it details the development of textiles and clothing products from recycled materials. Various aspects such as the classification of textile waste, recycling methods, various potential applications of recycled materials in the development of textile products, challenges, and the future prospects of the textile recycling industry are discussed.

"Environment Friendly Textile Processing Using Plasma and UV Treatment" deals with the processing of textiles using plasma and UV treatments. This chapter includes the details pertaining to the different surface modification methods of textile materials, different types of plasma and UV treatments, and their generation methods. Detailed discussions pertaining to the applications of these treatments in textile chemical processing and finishing stages of textiles and the clothing sector are presented. A comparative look at conventional processing, plasma, and UV treatments is also discussed along with highlighting the sustainability advantages of plasma and UV treatments.

"Sustainable Textile Wet Processing-Applications of Enzymes" is dedicated to the subject of enzymes and their applications in textile chemical processing. Enzymes, one of the important elements used in the textile sector today are a sustainable alternative to toxic textile chemicals used in the clothing sector. An overview of classification, advantages and disadvantages, and the mechanism of enzymes are presented here. Applications of enzymes in various textile processing steps are discussed in detail.

"Regenerated Cellulosic Fibers and Their Implications on Sustainability" deals with the sustainability aspects of regenerated cellulosic fibers. This chapter includes the present scenario, production technologies, properties, applications, and market trends of these fibers. Different sustainability issues pertaining to the production of regenerated cellulosic fibers are also presented.

"Application of Bio-Technology in the Processing of Textile Fabrics" talks about the applications of biotechnology in the textile sector. This wide subject has been dealt in detail in this chapter through various topics such as the overview of industrial biotechnology and its role in achieving a low carbon economy, green polymers, different enzymes used for bioprocessing, employment of biotextiles in various industrial textile applications, and the applications of biotechnology for the development of sustainable textiles.

"Jute-Based Sustainable Agrotextiles, Their Properties and Case Studies" deals with the details pertaining to jute-based agro textiles and its implications on sustainability. Jute is one of the important natural fibers being discussed widely under the fold of sustainable textiles. This chapter presents the properties of jute-based agro textiles and its associated case studies.

I would like to take this wonderful opportunity to thank all the contributors of different chapters included in this first roadmap volume of sustainable textiles and clothing for their incredible efforts in bringing out this book successfully with the enriched technical content in their chapters. I have no doubt that readers will certainly benefit from this book which brings out the important details associated with sustainable raw materials, processing methods, and techniques of the textile and clothing sector. This first roadmap volume on sustainable textiles and clothing will certainly become an important reference for the researchers and students, industrialists, and sustainability professionals working in this field.

Contents

Natural Plant Fibers: Production, Processing, Properties and Their Sustainability Parameters

Sohel Rana, Subramani Pichandi, Shama Parveen and Raul Fangueiro

Abstract This chapter discusses the present scenario and market trend of some important natural plant fibers such as cotton, flax, jute, and hemp. Production, processing, and applications of these fibers are discussed. The factors influencing the sustainability of these natural plant fibers are presented and various lifecycle assessment studies performed on these fibers to evaluate their environmental impacts and sustainability are discussed.

Keywords Natural plant fibers · Production · Processing · Application · Lifecycle assessment · Sustainability

1 Introduction

Natural plant fibers such as cotton, flax, hemp, jute, sisal, banana, coir, bamboo, and the like offer several benefits with respect to synthetic fibers such as abundance and low cost, renewability, eco-friendly, low-density and high specific properties, nonabrasiveness, and biodegradability. Some of these natural plant fibers such as cotton and linen, among others, provide excellent comfort to the garments and therefore, are very popular and extensively used in the apparel sector. However, due to lightweight, high specific mechanical properties and other

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attractive properties, the use of natural plant fibers in various industrial sectors such as leisure, automobile, medical, and building industries has increased approximately 13 % over the last 10 years and annual consumption is currently $\sim$275 million kg [1].

Natural plant fibers are usually considered more environmentally friendly than synthetic fibers for several reasons such as: the growth of plants results in sequestration of CO_2 from the atmosphere, natural plant cultivation consumes less energy than the production of synthetic polymers and fibers, natural fibers are produced from renewable resources unlike the production of synthetic fibers which leads to depletion of natural resources [1], and so on. Moreover, at the end of their lifecycle natural plant fibers are biodegradable. The main component of plant fibers is cellulose which can be broken down by microorganisms through enzymatic hydrolysis which involves multistage hydrolysis of cellulose into glucose [2]. Due to the above factors, natural plant fibers are generally considered to have much lower environmental impacts and to be more sustainable. However, cultivation and processing of natural plant fibers consumes more water, may use synthetic fertilizers and pesticides, and results in emissions of greenhouse gases in some processing stages. These are very important environmental aspects for these fibers and therefore, should be investigated thoroughly in order to understand their sustainability issues properly and to compare with those of synthetic fibers. In this context, this chapter presents the various issues related to the sustainability of some common natural plant fibers, namely cotton, hemp, flax, and jute. The present market scenario of these fibers, their properties, processing, and applications are also presented.

1.1 Present Scenario and Market Trend

Developing countries are now playing an increasingly greater role in the production, movement, and processing of cotton into finished products. In 2012–2013, developing countries account for most of the global cotton mill use (96 %), imports (97 %), and production (81 %), but they only account for 52 % of global cotton exports. Developing countries compete with developed countries such as the United States, Australia, and Greece for export markets. Developing countries, however, are not a homogeneous group. Economically powerful China, India, Brazil, and Turkey are playing a greater role in the market than most of the least-developed countries such as African cotton producers and a few Asian cotton-consuming countries. In total, the smaller economies represent only 5 % of global cotton production, 11 % of exports, 5 % of mill use, and 10 % of imports. One of the most important developments of the past decade is China's rise as the largest importer of cotton, accounting for 36 % of world cotton imports in 2012–2013. Bangladesh, Turkey, Indonesia, and Vietnam are the next largest importers, with a combined share of 30 % in 2012–2013, rising from 28 % existing five years ago due to increasing consumption. In contrast, Pakistan's share has decreased from 10 to 2 % in 2011–2012 due to reduced consumption, but rose to 5 % in 2012–2013.

Table 1 Top flax fiber producers in the world for the year 2011 [4, 6]

S. no.	Country	Production (metric tonnes)
1	Canada	368,300
2	China	350,000
3	Russia	230,000
4	India	147,000
5	United Kingdom	71,000
6	United States	70,890
7	Ethiopia	65,420
8	Kazakhstan	64,000
9	Ukraine	51,100
10	Argentina	32,170

The largest exporter of cotton over the last five years has been the United States, accounting for around one-third of global cotton trade. India was the second largest exporter in 2007–2008 with 19 % of global trade but its share has dropped to 10 % due to higher domestic mill use. Central Asia's share has also decreased (from 16 to 10 %) due to reduced production and increased consumption. The shares of Brazil and the C-4 countries (Benin, Burkina Faso, Chad, and Mali) have risen from 6 to 11 % and from 3 to 6 %, respectively) due to higher production. Australia's share rose from 3 to 12 %, also from increased production. Brazil, India, and Uzbekistan export large enough quantities to have a potential impact on global cotton prices, whereas smaller African countries are mainly price-takers. Over the last decade, the destination of cotton exports has switched from Europe to Asia, and in particular to China. The previous relative advantage of African countries regarding freight time and cost, compared to exporters such as India, Central Asia, and Australia, has disappeared. Currently Africa is one of the farthest providers of cotton to Asia. However, intermediate export locations such as Malaysia have recently developed; the merchants ship cotton there to better answer the short-notice demands from Asian countries [3].

India, Bangladesh, China, Uzbekistan, and Nepal are the major jute-producing countries in the world. Among these countries, the topmost jute producers are India and Bangladesh, which produced 3,447,641 tonnes of jute fibers in 2011, out of the total world production of 3,583,235 tonnes. India produced 2,053,206 tonnes of jute in 2012–2013 [4, 5]. Flax fibers are produced in the cold countries. In 2011, the global flax fiber production was 1,602,047 tonnes. Table 1 provides the production of top 10 flax-producing countries [6].

Currently, hemp fibers are mainly produced in about 30 countries in Europe, Asia, and North and South America. Among these countries, the largest share in producing and exporting hemp textiles and products is from China. France, the United Kingdom, Romania, and Hungary are the main hemp-producing countries in the European Union (EU). Other countries producing (and/or consuming) hemp actively are Russia, Ukraine, Switzerland, Australia, New Zealand, India, Japan, Korea, Turkey, Egypt, Chile, and Thailand. Hemp was produced globally on about 200,000 acres of land in 2011 producing more than 380 million pounds. The

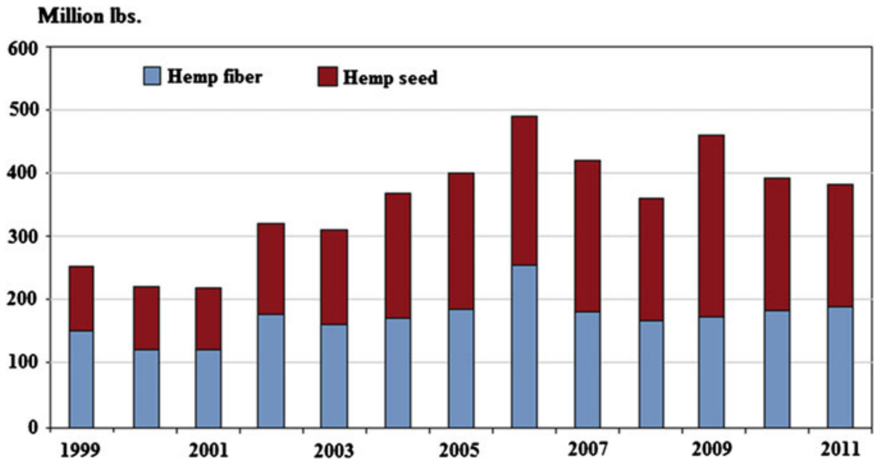

Fig. 1 Hemp fiber and seeds global production (1999–2011) [9]

production of hemp in 1999 was about 250 million pounds and production has mainly increased due to increasing production of hemp seed [4, 7–9], as shown in Fig. 1.

2 Properties of Natural Plant Fibers

2.1 Cotton Fiber

Cotton is a cellulosic fiber obtained from natural sources. Cotton fiber grows in a ball around the seeds of the cotton plant of the genus *Gossypium* (see Fig. 2) and are soft and fluffy staple fibers. However, cotton fiber quality is strongly influenced by the grade, color, length, and characteristics of the fiber. The countries that produce most of the cotton fiber are the United States, India, China, Egypt, Pakistan, Sudan, and Eastern Europe.

External appearance, brightness, and color are the important criteria for the gradation of cotton fiber. The color of raw cotton is normally white or gray but other colored varieties are also available such as reddish, chamois, and tawny, among others. The cotton fiber quality is most strongly influenced by the length that divides cotton fiber into two major categories: long staple fiber having a length more than 28 mm and short staple fiber having a length shorter than 28 mm. Sea Island, Egyptian Giza, Pima, and so on are long staple fibers, whereas the varieties of cotton usually grown in Asian countries are short staple fibers. Cotton fibers having good strength characteristics are considered as good quality cotton for practical applications [10–15].

Fig. 2 Cotton fiber [12]

2.1.1 Properties of Cotton Fiber

Table 2 provides the gradation of cotton fiber according to various quality characteristics [11–22].

Physical properties of cotton fibers are given below:

- Color: White, creamy white, bluish white, yellowish white, or grey.
- Tensile Strength: Moderately strong fiber with a tenacity of 3–5 g/d. The wet strength of cotton fiber is 20 % higher than dry strength.
- Elongation at break: Doesn’t stress easily and it has an elongation at break of 5–10 %.
- Elastic recovery: Rigid and inelastic fiber. At 2 % extension it has an elastic recovery of 74 % and at 5 % extension it has an elastic recovery of 45 %.
- Fiber density: 1.54 g/cm^3.
- Moisture regain: 8.5 %.
- Effect of heat: Excellent resistance to thermal degradation. The fiber turns yellow after several hours of heating at 120 °C, decomposes markedly at 150 °C, and is severely damaged after a few minutes at 240 °C. Cotton burns in air.
- Effect of sunlight: Turns yellow when exposed to sunlight and starts losing strength gradually due to the action of UV light and short wave lengths of visible light.
- Effect of age: Shows slight loss of strength when stored carefully. After 50 years of storage cotton may differ only slightly from the new fibers.

2.1.2 Chemical Properties of Cotton Fiber

- Effect of alkalis: Cotton fiber has excellent resistance against alkalis. The fiber swells in caustic soda (NaOH), but doesn’t get damaged. Treatment of cotton with caustic soda leads to improvement of luster and strength of the fiber (mercerization process).

Table 2 Grading of cotton fiber according to various quality parameters [12]

Fiber property	Description
Length (upper half mean length, in.)	
Below 0.99	Short
0.99–1.10	Medium
1.11–1.26	Long
Above 1.26	Extra long
Uniformity index (%)	
Below 77	Very low
77–79	Low
80–82	Low
83–85	High
Above 85	Very high
Fiber fineness (millitex)	
Below 135	Very fine
135–175	Fine
175–200	Average
200–230	Coarse
Above 230	Very coarse
Fiber strength (1/8 in. gauge strength in g/tex)	
20 and Below	Very weak
21–25	Weak
26–29	Average
30–32	Strong
32 and above	Very strong
Fiber elongation (%)	
Below 5.0	Very low
5.0–5.8	Low
5.9–6.7	Average
6.8–7.6	High
Above 7.6	Very high
Fiber maturity (maturity ratio)	
Below 0.7	Uncommon
0.7–0.8	Immature
0.8–1.0	Mature
Above 1.0	Very mature

- Effect of acids: Cotton fiber is damaged and disintegrated by cold concentrated acids or even hot diluted acids. It is not affected by weak acids in cold conditions. Cotton can be dissolved in concentrated 70 % sulfuric acid.
- Effect of organic solvents: Cotton has good resistance against organic solvents used for cleaning. Copper complexes, such as cuprammonium hydroxides, cupriethylene diamine, and the like can dissolve cotton fiber.
- Effect of microorganisms: bacteria, fungi, and mildews can attack cotton fiber and hot and humid conditions are favorable for their growth. Weakening of cotton materials can result due to the growth of microorganisms.

Table 3 Physical properties of jute fiber [29]

S. no.	Properties	Description
1	Fiber tenacity	3–4 g/d
2	Elongation at break	1.7 %
3	Fiber diameter	0.015–0.020 mm
4	Fiber density	1.50 g/cc
5	Moisture regain	13.75 %
6	Resiliency	Bad
7	Dimension stability	Good
8	Abrasion resistance	Average
9	Effect of light and heat	Average
10	Effect of microorganisms	Good (better than cotton)

2.2 Jute Fiber

Jute is a type of bast fiber extracted from the stem of the jute plant, having long length and soft with a shiny appearance. Jute is the cheapest natural fiber and is considered the golden fiber due to its color and cash value. Jute fiber is mainly composed of cellulose, lignin, and pectin. China, India, and Bangladesh are the main producers of jute in the world. Warm and humid conditions are suitable for the growth of jute plants. Gradation of jute fiber is made according to its color, strength, and fiber length. Jute fibers are usually off-white to brown in color and have length in the range of 0.9–4.5 m [23–28].

2.2.1 Physical Properties of Jute Fiber

The physical properties of jute fiber are given in the Table 3.

2.2.2 Chemical Properties of Jute Fiber

- Effect of acids: Cold concentrated acids damage jute fiber. Dilute acids can damage in hot conditions [24, 29].
- Effect of alkalis: Strong alkalis damage jute fibers leading to loss of weight.
- Effect of bleaching agents: Jute has very good resistance against beaching agents.
- Effect of light: Sunlight slightly changes the color of jute fiber due to the presence of lignin.
- Effect of mildew: Resistance is better than cotton and linen.
- Dyeing ability: Easily dyeable; usually dyed by basic dyes [24, 29].

2.3 Linen Fiber

Linen fibers are extracted from flax plants and originated in the Mediterranean region of Europe (Swiss lake region). The Soviet Union, Poland, and France are the main producers of linen in the world. Linen fiber contains about 70 % cellulose. This fiber has anti-allergic characteristics, good moisture absorbency, and allows the skin to breathe. This fiber has low elasticity and resiliency, making the deformation of linen fabrics difficult [30–34].

2.3.1 Physical Properties of Linen Fiber

The physical properties of linen fiber are provided below:

- Color: Yellowish to grey.
- Length: 18–30 in.
- Tensile strength: Stronger than cotton fiber, tenacity in the range of 5.5–6.5 g/den.
- Elongation at break: 2.7–3.5 %.
- Elastic recovery: Very less.
- Fiber density: 1.50 g/cm^3.
- Moisture regain: 10–12 %.
- Effect of heat: Excellent thermal resistance, better than cotton fiber.
- Effect of sunlight: Shows good sun light protection.
- Resiliency: Very poor.
- Luster: Brighter than cotton fiber and slightly silky.

2.3.2 Chemical Properties of Linen Fiber

- Effect of acids: Damaged highly only by concentrated acids, not by dilute acids if washed immediately [31, 33, 35–38].
- Effects of alkalis: Linen has excellent resistance against alkalis.
- Effect of bleaching agents: Chlorite and hypochlorite bleaching agents do not affect linen fiber in cold conditions.
- Effect of organic solvents: Good resistance against organic solvents.
- Effect of insects: Resistant against moth-grubs or beetles.
- Effect of microorganisms: Similar to cotton.
- Dyes: Can be dyed with direct and vat dyes.

2.4 Hemp Fibers

Hemp is a bast fiber extracted from the stalk of hemp plants that grow well in the soils which are well drained, rich in nitrogen, and nonacidic. Hemp plants are advantageous as they need less pesticide due to their very fast growth attracting fewer pests [30, 39–43].

2.4.1 Physical Properties of Hemp Fiber

- Color: From yellowish grey to deep brown.
- Length: 4–6.5 feet.
- Tensile Strength: A very strong fiber (250 MPa for 66 μm).
- Elongation at break: Hemp fibers stress easily.
- Elastic recovery: Elastic recovery is very poor, even less than linen fiber.
- Moisture regain: 12 %.
- Effect of heat: Excellent resistance to thermal degradation.
- Effect of sunlight: Sufficient resistance against sunlight.
- Luster: Highly bright similar to linen fiber.

2.4.2 Chemical Properties of Hemp Fiber

- Effect of acids: Similar to cotton fiber, hemp is attacked and disintegrated by hot dilute acids or cold concentrated acids [35, 39, 41, 42, 44, 45].
- Effect of alkalis: Has excellent alkali resistance.
- Effect of organic solvent: Resistant against organic solvents.
- Effect of insects: Resistant against moth-grubs or beetles.
- Effect of microorganisms: Similar to cotton fiber.
- Dyes: Dyeing is difficult.

3 Production Process of Natural Plant Fibers

3.1 Cotton Fiber

3.1.1 Cultivation

The requirements for the cultivation of cotton plants are long frost-free periods, more sunlight, moderate rainfall (annual rainfall about 60–120 cm), and fairly heavy soils containing a moderate level of nutrients. Although seasonally dry tropical and subtropical regions of the northern and southern hemispheres present ideal growing conditions for cotton, it is grown in large quantities nowadays in regions with less rainfall through the use of irrigated water. Cotton seeds are sown from the beginning of February to the beginning of June. South Plains is the region of the United States which is known as the largest contiguous cotton-growing region in the world.

3.1.2 Harvesting

In past, manual harvesting of cotton was the common practice. However, nowadays, this is done efficiently using machines called strippers and pickers. Spindle harvesters or pickers can remove cotton from the bolls simultaneously from two rows using spindles attached to a drum. Pickers are highly efficient and using only one row can perform the work of 40 hand pickers. In the case of the stripper machine, cotton as well as twigs and leaves are removed from the cotton plants by passing them between revolving rollers or brushes. Ginning machines (roller and saw gins) are then used to separate seeds from the cotton fibers. After removal of seed coats, cotton is pressed to produce bales of standard weight [12, 15, 46].

3.1.3 Impact of Cotton Fiber Production on Sustainability

Cotton fiber is considered as sustainable as it is renewable, biodegradable, and environment friendly throughout its entire lifecycle. Important sustainability parameters involved in cotton fiber production are soil, water, land, energy, and air quality, as discussed below.

- Cotton fiber cultivation can affect the soil due to land preparation leading to soil erosion, and due to use of various chemicals such as insecticides and pesticides. However, new technologies of cotton cultivation using conservation tillage avoids mixing and disturbing soil to a much lesser extent and thereby prevents soil erosion as well as leads to soil creation, by planting winter or cover crops. Moreover, cotton is being cultivated nowadays using much smaller quantity of insecticides and pesticides (according to the US Department of Agriculture, 1.2 lbs/acre insecticides and 2.1 lbs/acre pesticides are used for each acre of cotton). In the United States, 0.09 oz of total pesticides are used to produce 1 pound of cotton. A decreasing trend in the use of chemicals to grow cotton can be observed throughout the world and currently, cotton needs only 8.5 % of total pesticides used to grow various crops.
- Cotton plants can tolerate dry conditions and heat and do not need a large quantity of water. In many regions of world, water from natural resources such as rainfall is sufficient for the cultivation of cotton and, therefore, is associated with very small environmental impacts.
- The use of land for the cultivation of cotton has decreased considerably through the use of modern agricultural technologies. Production of 50 % more cotton than that produced 40 years ago on the same land is possible nowadays using these modern technologies.
- Air pollution is an important parameter during the production of cotton fiber and the ginning process. The dust emission from the field has been reduced as a result of using modern technologies such as reduced tillage. Moreover, many quality control measures are followed to reduce the emission of dust in the

ginning process. Besides reducing dust emissions, these modern techniques also reduce CO_2 emission considerably.

- In modern times, the energy requirements for cotton production are balanced through the production of biofuel from cotton seeds [47, 48].

3.2 Production of Jute Fiber

Jute seeds are scattered by the farmers on cultivated soil to grow jute plants. Jute plants are harvested after four months when they flower but before the flowers go to seed. Jute stalks are then cut off near the ground, tied into bundles and soaked in water for retting for a period of 20 days. The process of extracting bast fibers from the stem of plants is known as the retting process. Different types of retting processes are: mechanical retting (hammering), chemical retting (boiling and applying chemicals), steam/vapor/dew retting, and water or microbial retting. Although very old, water or microbial retting is the most popular and widely used method of extracting fine jute fibers. Due to softening of the tissues and rupture of the hard pectin holding the jute fibers and inner woody sticks, the retting process allows the jute fibers to be separated from the stalks. After washing the stripped long strands of jute fibers in clear running water they are dried by hanging or spreading over the roofs for two to three days, and subsequently tied into bundles. A warm and wet climate with temperatures ranging from 70–100 °F, relative humidity of 70–80 % and weekly 2–3 in. of rainfall (some more during sowing) is suitable for the cultivation of jute fibers [24, 26, 49–51].

3.2.1 Impact of Jute Fibers Production on Sustainability

Some important aspects of jute fiber production related to sustainability are as follows:

- Jute fibers are produced from annually renewable resources. Cultivation leads to a high biomass production per unit of land area. Jute harvesting can be done within 4–6 months, producing a much higher quantity (40 tonnes of dry stem per hectare) as compared to wood. The higher biological efficiency of jute plants than wood will greatly reduce the cost of paper production using jute instead of wood and also reduce the need for cutting down trees, that is, deforestation.
- Jute can be grown naturally without the use of chemical fertilizers. The shedding of jute leaves during the growing season and leftover crop waste are transformed into organic matters and thereby enrich the soil with nutrients. Therefore, supplementary chemical fertilizers are not required for the subsequent crops and the fertility level of the soil is sustained.

- According to several studies, the CO_2 assimilation rate of jute is several times higher than other trees and CO_2 emissions during transportation and milling of jute fiber is one-sixth of that emitted during the manufacturing process of PP fiber.
- Various organic chemicals and gases are generated during the production of jute fibers such as acetone, ethyl alcohol, butyl alcohol, methane, carbon dioxide (CO_2), and hydrogen sulfide, among which CO_2 and methane are the main substances causing global warming. Methane, which is emitted during the retting process of jute, is known to have more global warming potential as well as more harmful as an ozone-depleting agent than CO_2. Generation of methane gas can be significantly suppressed using ribbon retting of jute and, therefore, its large-scale adoption will improve the sustainability of jute fibers. Also, another new method of retting developed in China, known as humidified retting, is very helpful in reducing water pollution, use of water, and emission of methane.
- When jute plants are produced in rotation with other crops, it has been noticed that jute planting can improve the health of these crops as well as reduce the risk of pest attack and infestation of diseases [23, 25].

3.3 Production Process for Linen Fiber

The cultivation of flax plants usually takes about 100 days from the planting of seed up to the harvesting stage. First, the land is plowed in the spring and then turned into a good seedbed through discing, harrowing, and rolling. Flax seeds need to be planted shallowly and covered with soil. Seeds can be distributed manually or machines can also be used to plant the seeds in rows. After the required growth period, seeds are first collected from the plants and then the plants are subjected to the retting process. The common methods of retting flax fiber are (a) dew retting in which flax fibers are spread over the field and retting is carried out through the actions of dew, rain, and sun along with soil-borne bacteria, and (b) water retting in which flax fibers are submerged in water for a time period of 6–20 days and retted due to the actions of bacteria. The water retting method is nowadays being considered to be expensive. After retting, flax fibers are extracted from the stems using the scutching process in which flax fibers are moved on the long tables to remove impurities and further threshed to extract the fibers. In the scutching process, flax fibers are divided into finer fibers called line, shorter fibers or tow, and shives or the woody part. Fine fibers are then converted to slivers by hackling and then weighed, manually sorted, and packed in the form of bales or rollers weighing 100 kg [30–32, 52].

3.3.1 Impact of Production Process of Linen on Sustainability

The following strategy can be followed during the production of flax fibers to improve their sustainability aspects:

- Use of minimal or shallower plowing, in which the energy requirement is considerably less and advantageous particularly on a sloping field due to less soil erosion or runoff of soil sediments.
- Use of no-till and water retting which has lower environmental impact potential. Moreover, the use of warm water retting can reduce the energy requirement significantly.
- The use of coproducts such as short fiber and shives in animal bedding or in paper production. Dusts produced from the scutching and hackling process can be collected and consolidated as biomass fuel [52, 53].

3.4 Production Process of Hemp Fibers

Hemp is an annual plant that grows from seeds in varieties of soils, which are well drained, rich in nitrogen, and nonacidic. The best land for producing hemp is the land that gives high yields of corn. A mild climate, humid atmosphere, and a rainfall of at least 64–76 cm per year are suitable conditions for the growth of hemp plants. For the plantation of hemp seeds, the preferred soil temperature is 5.5–7.7 °C. Harvesting of crops begins after 70–90 days of seeding when the plants start to shed pollen. Commonly, a special machine with rows of independent teeth and a chopper is used for harvesting. After the harvesting of the crop, the stalks are retted by spreading them in the field for four to six weeks, depending on the weather. During this period, most of the nutrients extracted by the plant are returned to the soil due to the decomposition of the leaves. To ensure the evenness of the retting process, the stalks are turned several times using a special machine and subsequently, the extracted fibers are baled and stored in dry places [40–43, 54, 55].

3.4.1 Impact of Production Process of Hemp Fiber on Sustainability

Hemp fiber cultivation is considered to be sustainable due to the following facts:

- Hemp nuts used in modern hemp-based products (e.g., TemptHemp) are pesticide- and herbicide-free.
- Hemp plants do not lead to depletion of soil unlike many industrial crops. Enrichment of soils occurs due to hemp plants as they throw out their leaves to soils throughout the whole growing season and thereby produce a mature compost. This leads to enrichment of soils as well as retention of soil moisture,

also due to the fact that hemp requires only 50 % of water used by other agricultural crops.
- Hemp plants help to maintain a strong soil structure and therefore, protect soils from runoff due to their deep roots of at least three feet under the ground.
- Hemp cultivation removes heavy metals from soils leading to soil purification.
- Hemp acts as a carbon sink due to absorption of CO_2.
- Hemp fiber production is an efficient process; it is possible to get 250 % more fiber than cotton and 600 % more fiber than flax per acre.
- Hemp has diversified applications including: paper, textiles, biodegradable plastics, construction (i.e., hemp concrete that helps sequester CO_2, insulation, paneling, etc.), natural foods, fuel, medical purposes, automobile door panels, body care products, household products (i.e., cleansers, inks, varnishes, etc.), animal feed, animal bedding, and as a hydrocarbon absorbent [41].

4 Applications of Natural Plant Fibers

4.1 Applications of Cotton Fiber

The major applications of cotton fiber are [12, 13]:

- Apparel sectors, home furnishings such as draperies or professional garments and other industrial uses (such as medical supplies).
- Cotton fabrics with specialty applications include: fire-proof (flame resistant) apparel and wrinkle-free apparel.
- Cotton also finds specialty applications in medical and hygienic uses, such as hydrophilic cotton (cotton wool), compress, gauze bandages, tampons or sanitary napkins, and cotton swabs.

4.2 Applications of Jute Fiber

- *Medical Applications* Nonwoven jute fabrics with antibacterial finishes for medical wear and other sterile applications [24, 28, 51] .
- *Home Textiles* For a wide range of home textiles, including bed sheets, cushions, tablecloths, tableware, carpets, and wallpaper.
- *Building Materials*. Jute can be used to produce chipboard and other composites (pseudo-wood) for use in building construction. Also, jute fibers can be used to improve insulation in buildings.
- *Structural Composites*
  - Building material: False ceiling, panel, partitions, doors and windows, furniture, and prefabricated shelters.

  - Automobile components: Auto trims, interiors, dashboard panels, panels for railways coaches, and the like.
  - Engineering components: Brake liners, moulding materials, and so on.
  - Other applications—Packing boxes, sign boards, and letter boxes among others.

- *Automotive Textiles* Jute felts are used for auto interiors in seat backing and auto carpet underlay and in the form of composites in door panels, dashboards, head liners, brake linings, parcel shelves, auto trims, and the like.
- *Protective Textiles* For aprons and gloves with special fireproof and oil- and water-repellent finishes to protect those working in oil refineries, fire brigades, refractors, and engineering plants.

4.3 Applications of Linen Fiber

- Linen fibers are used to produce bed and bath fabrics such as tablecloths, dish towels, bed sheets, and so on, home and commercial furnishing items (wallpaper/wall coverings, upholstery, window treatments, etc.), apparel items (suits, dresses, skirts, shirts, etc.), industrial products (luggage, canvases, sewing thread, etc.) [29, 50].
- Linen handkerchiefs are used to decorate men's suits.
- Linen/cotton blended yarns are presently being produced for use in denim to improve its feel in hot and humid weather.
- Linen fabric is traditionally used as the support for oil painting due to its better strength, durability, and archival integrity as compared to cotton.
- Linen cloth is used by bakers to hold the dough in shape before baking.

4.4 Applications of Hemp Fiber

Hemp is used for a wide variety of purposes including [56, 57]:

- Manufacturing of cordage of varying tensile strength, durable clothing, and nutritional products.
- Blends of hemp with flax, cotton, or silk are used for apparel and furnishings.
- Hemp is commonly used in nonwoven items and other industrial applications such as mulch, animal bedding, and litter.
- Hemp is used for industrial purposes including paper, textiles, clothing, biodegradable plastics, construction, body products, and the like.
- Hemp is commonly used to make sail canvas.

Table 4 Comparison of 1 kg conventional seed cotton cultivation and organic seed cotton cultivation using CML 2001 (all impact categories) V2.05/world. 1995—characterization. (including long-term emissions) [58]

Impact category	Unit	Conventional seed cotton cultivation	Organic seed cotton cultivation
Abiotic depletion	Kg Sb eq.	0.012065	0.009334
Acidification	Kg SO_2 eq.	0.011553	0.006783
Eutrophication	Kg PO_4 eq.	0.002898	0.001952
Global warning 500 a	Kg CO_2 eq.	1.329722	1.080763
Ozone layer depletion steady state	Kg CFC–11 eq.	8.96E–08	5.85E–08
Human toxicity infinite	Kg 1,4–DB eq.	1.118018	0.932881
Freshwater aquatic ecotoxicity Infinite	Kg 1,4–DB eq.	0.479644	0.384923
Terrestrial ecotoxicity infinite	Kg 1,4–DB eq.	0.010375	0.009473
Freshwater sediment ecotoxicity infinite	Kg 1,4–DB eq.	1.025340	0.825297
Land competition	m^2a	0.146766	0.147047
Photochemical oxidation	Kg C_2H_4	0.000536	0.000333

5 Sustainability Studies on Natural Plant Fibers

5.1 Lifecycle Assessment of Cotton Fiber

Lifecycle assessment is an important tool that has been used for textile fibers to investigate their sustainability aspects. A few studies have been conducted employing LCA to investigate the environmental impact of cotton fiber. A cradle-to-gate LCA analysis was performed by Murugesh Babu et al. to investigate the environmental impacts of cultivation of conventional as well as organic seed cotton fibers [58]. Within this study, a functional unit was defined as the cultivation of 1 kg of conventional and organic seed cotton fibers and the system boundary included all stages of production from cultivation to harvesting of seed cotton fibers, production and transportation of fertilizers and pesticides, irrigation use, and electricity consumption for irrigation. Table 4 provides the environmental impacts for the cultivation of 1 kg conventional seed cotton and organic seed cotton.

It can be observed that conventional seed cotton cultivation leads to higher environmental impact as compared to organic seed cotton. The use of plant protection chemicals (e.g., pesticides, herbicides, and synthetic fertilizers) and irrigation are the primary reasons for higher environmental impacts in the case of conventional seed cotton cultivation. Freshwater sediment ecotoxicity, freshwater aquatic ecotoxicity, terrestrial ecotoxicity, abiotic depletion, global warming, acidification, and eutrophication are the dominating environmental impacts in the case of conventional seed cotton and these result from the use of irrigation, plant protection chemicals, fertilizers, and fossil fuel consumption during tillage and

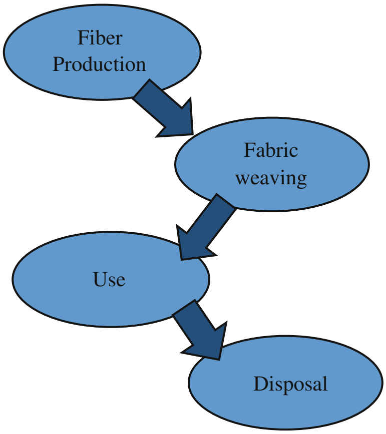

Fig. 3 Flow chart showing different stages of the cotton and polyester fiber lifecycle [59]

transportation of plant protection chemicals and fertilizers from the manufacturing unit to the field. The primary source of environmental impact is irrigation as a large quantity of water (2.6174 m^3/kg of seed cotton) is used during the cultivation of seed cotton. The use of pesticides has many detrimental effects such as harm to the health of laborers, contamination of cottonseed and cottonseed derivatives (which is an important source of edible oil), build-up of resistance in pests, harm to the beneficial fauna, pollution of surface water as well as of groundwater, and so on. Moreover, synthetic nitrogen fertilizer is also responsible for nitrous oxide emission, and phosphate fertilizers lead to the accumulation of heavy metals in the soil as well as surface water eutrophication. In contrast to conventional seed cotton, the factors responsible for environmental impacts in the case of organic cotton are the use of irrigation, tillage and mineral fertilizer (potassium chloride), and transport. In both cases, use of irrigation and land are the same and irrigation is the primary source contributing to the overall environmental impacts.

Also, sustainability of cotton fiber with other fibers, for example, polyester fibers has been compared using LCA. The lifecycle of fiber involves different stages such as fiber production, fabric forming, and usage and disposal of products, as presented in the flowchart, shown in Fig. 3 [59].

5.1.1 Fiber Production

The sources and inputs involved in cotton and polyester fiber production are provided in Table 5.

Table 5 The factors involved in cotton and polyester fiber production (for 1 kg fiber/fabric) [59]

	Polyester	Cotton
Energy	97 MJ	60 MJ
Oil or gas	1.5 kg	–
Fertilizers	–	457 g
Pesticides	–	16 g
Water	17 L	22,200 L
Carbon dioxide emissions	2.3 kg	3.0 kg
Approximate cost	£0.78	£1.13

Table 6 The inputs and outputs involved in cotton and polyester fabric weaving (for 1 kg fabric) [59]

	Polyester	Cotton
Energy	33 MJ	40 MJ
Water	1,291 L	3,900 L
Carbon dioxide emissions	1.5 kg	2.3 kg

Table 7 The factors involved during usage of 1 kg polyester and cotton fabric [59]

	Polyester	Cotton
Energy per wash	3.4 MJ	3.4 MJ
Energy per dry	Cannot tumble dry	12.6 MJ
Shrinkage (100 washes)	4 %	7 %
Loss of strength (100 washes)	8 %	17 %
Water per wash	49 L	49 L

5.1.2 Fabric Weaving

The energy and water used in cotton and polyester fabric weaving as well as CO_2 emission are presented in Table 6.

5.1.3 Product Use

The factors involved using cotton and polyester fiber products such as fabric are given in Table 7.

5.1.4 Product Disposal

Table 8 lists the factors involved during disposal of cotton and polyester fiber products.

According to the data provided in Tables 5, 6, 7, 8 and 9, the sustainability aspects of cotton and polyester fiber can be summarized. Table 9 shows the performance of 1 kg of cotton and polyester fabrics over a lifetime of two years, which

Table 8 Energy required during disposal of 1 kg polyester and cotton products [59]

	Polyester	Cotton
Energy recovery from incineration	33 MJ	7 MJ
Biodegradability	No	Yes
Carbon dioxide from landfill	–	5.5 kg
Recyclability	Yes	Yes

Table 9 Performance of 1 kg of cotton and polyester fabrics over a period of two years [59]

Energy	Polyester uses 171.5 mJ of energy Cotton uses 140.1 mJ of energy	Cotton ✓
Oil and gas	To produce 1 kg of polyester, it takes 1.53 kg of oil or gas. Organic cotton grows naturally	Cotton ✓
Fertilizers and pesticides	Growing 1 kg of cotton uses 457 g of fertilizers and 16 g of pesticides. In the case of organic cotton, chemicals are not used but this is less common	Polyester ✓
Emissions	1 kg of polyester is responsible for 3.8 kg of carbon dioxide whereas cotton causes 5.3 kg Sulfur dioxide causes acid rain. Cotton results in 4 g and polyester 0.2 g	Polyester ✓
Water	Polyester uses 1,900 L (including washes). In the case of cotton, 1 kg requires 26,700 L of water during its life	Polyester ✓

includes 12 washes. It can be observed that the production and use of cotton fabrics use less energy as well as natural resources such as oil and gas as compared to polyester fibers. However, the use of fertilizers and pesticides, CO_2 and SO_2 emissions, and water use are the main concern for cotton fiber affecting its sustainability. However, as discussed in the section “Impact of Cotton Fiber Production on Sustainability,” it is possible to reduce the impacts of these factors using modern agricultural practices, in order to improve the sustainability of cotton fiber.

The inventory calculations proved that cotton fiber production consumes about 40 % less energy than polyester fiber production. Cotton growing requires, however, huge amounts of water: irrigated amounts vary from 7 to 29 tonnes per kg of raw cotton fibers. Pesticides and fertilizers used in traditional cotton cultivation have ecotoxic effects in contrast to organic cotton cultivation, where natural alternatives to agrochemicals are used.

Similar observations were also made by Kalliala et al. [60]. In their work, the LCA study was performed on conventional cotton, organic cotton, and polyester fibers in order to evaluate their environmental effects. Their study also reported that cotton fiber production consumes about 40 % less energy as compared to polyester fiber production. Also, the irrigation water consumed in cotton fiber production varies between 7–29 m^3/kg, whereas approximately 17 l/kg of water is consumed in polyester fiber production. Although organic cotton is beneficial due

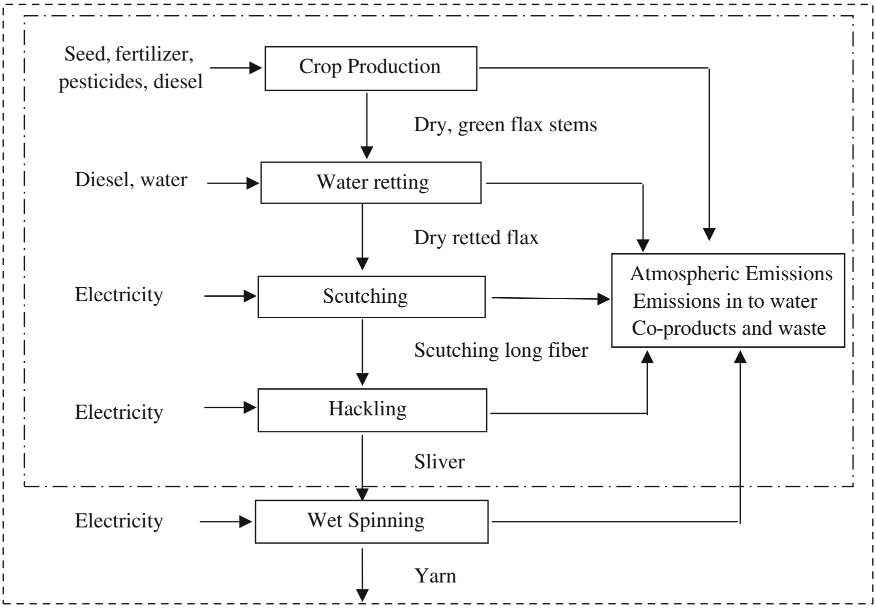

Fig. 4 System boundaries for flax sliver and yarn production [53]

to the lack of use of synthetic fertilizers and pesticides that cause harmful effects, it cannot be considered yet as a global alternative to conventional cotton because its production is currently only 0.03 % of total cotton production.

5.2 Lifecycle Analysis of Flax Fiber

Similar to cotton fiber, an LCA study has also been performed on flax fibers. This study includes all the stages starting from the farm gate up to the factory gate (Fig. 4). The use of fertilizers (N, P, and K) and pesticides was considered, whereas machinery/equipment construction, production of seed, transportation, storage, and manpower were not taken into account. Only the long fibers were counted as the products of high economic value and the various coproducts such as short fiber, shive, dust, and coarse plant residues were not considered to have any economic value except covering their processing costs after their separation from the reinforcement fibers. The disposal costs of these coproducts, therefore, were not included [53].

5.2.1 Crop Production

Crop production involves all agricultural operations such as plowing, harrowing, cultivating, applying fertilizer, pesticides, and desiccants and harvesting. It can be noticed that the type of plowing technique is an important sustainability factor for

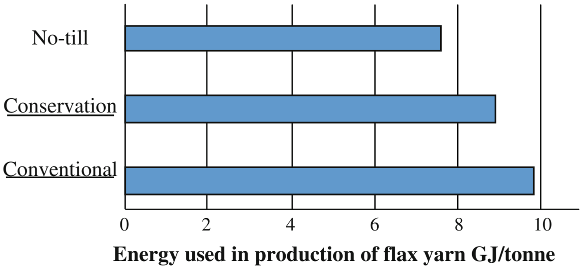

Fig. 5 Energy used in the production of flax yarn through different tillage practices [53]

the production of flax fibers and three different methods of plowing (tillage) practices such as conventional tillage, conservation tillage, and no-till have different energy requirements, as shown in Fig. 5 [53, 61]. It is evident from Fig. 5 that among these tillage practices, no-till is the most favorable technique in terms of energy requirements, whereas the conventional tillage method consumes the highest amount of energy.

5.2.2 Fiber Processing Operations

Fiber harvesting is followed usually by scutching/decortication, which is then followed by hackling and/or carding, which produces sliver. The retting process is another important parameter influencing the sustainability of flax fiber. The three different retting techniques such as warm-water retting, bioretting, and stand/dew retting have different energy requirements. The energy consumed in these retting techniques and subsequent scutching process is provided in Fig. 6. It is clear that the highest amount of energy is consumed in the bioretting process. On the contrary, warm-water retting can significantly reduce the energy requirement during flax fiber production.

5.2.3 Impacts of Crop Production and Fiber Processing

As mentioned previously, the energy requirement is considerably less in the case of minimal or shallower plowing, which is advantageous particularly on a sloping field due to less soil erosion or runoff of soil sediments. On the contrary, conventional tillage methods of mould board plowing is highly detrimental to the soil structure and leads to the break-up of natural aggregates and covers up the residues of the previous crop. This leads to more chance of soil erosion as the soil becomes unprotected and more exposed to the action of wind and rain. The energy requirement for chisel plowing is 40 % less than mould board plowing, whereas only 6 % of the energy required for mould board plowing is used in the case of drilling combined with a no-till pass. Herbicides applied as desiccant in stand/dew retting require almost 36 % of the total energy consumption at this stage. The most energy-intensive retting technique is bioretting which also includes postharvest

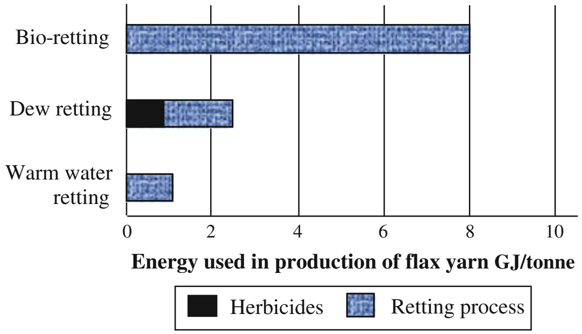

Fig. 6 Energy consumption in different retting and subsequent scutching processes [53]

field operations, scutching, rinsing, drying, and mechanical softening to produce long fibers. Although warm-water retting consumes the least energy among the various retting techniques, it leads to a large amount of wastewater (~94 % of water used). For producing one tonne of sliver and yarn, the total energy requirements are 59.3 GJ and 85.4 GJ, respectively, in the case of no-till and water retting and 199 GJ and 231 GJ, respectively, in the case of conventional method (mould board plowing) and bioretting. If these values are compared with energy requirements for one tonne for continuous glass fiber (25.8 GJ) and for one tonne of glass fiber mat (54.7 GJ), it is seen that the flax sliver produced through the low-energy route consumes energy similar to that for glass fiber mat [53, 61]. The input and output data for the production of one tonne of flax yarn using the least energy-consuming plowing and retting practices are presented in Table 10.

5.2.4 Environmental Impacts

LCA has been used to assess eight types of environmental impacts, namely, global warming potential (GWP), human toxicity potential (HTP), acidification potential (AP), eutrophication potential (EP), aquatic toxicity potential (ATP), nonrenewable/abiotic resource depletion potential (NRADP), ozone depletion potential (ODP), and photochemical oxidants creation potential (POCP). Environmental impacts for the production of one tonne of flax silver and yarn considering four possible types of tillage and retting processes are calculated as shown in Tables 11 and 12. Within this study, the system boundary starts from the farm gate to the factory gate and includes the production of agricultural products such as fertilizers and pesticides. However, this study does not consider the agricultural machinery/equipment construction, production of seed, transportation, storage, and manpower as well as the location, land use, and effects of crop rotation. The assumptions are: no difference in soil quality and quantity between the beginning and end of the study, long fibers are the high-value products, and coproducts such as short fiber, shive, dust, and coarse plant residues have economic value covering only their processing costs. Nonrenewable/abiotic resource depletion potential (NRADP)

Table 10 Inventory data for the production of flax fiber yarn using no-till practice and warm water retting [51]

Inputs		
Materials	Value	Units
Seed	497	Kg/tonne of yarn
Lime	2,445	Kg/tonne of yarn
Ammonium nitrate (N)	445	Kg/tonne of yarn
Triple superphosphate (P)	238	Kg/tonne of yarn
Potassium chloride (K)	368	Kg/tonne of yarn
Pesticides	9.4	Kg/tonne of yarn
Diesel	9.49	GJ/tonne of yarn
Electricity	35.52	GJ/tonne of yarn
Outputs		
Yarn	1,000	kg
Coproducts: short fiber	4,497	Kg/tonne of yarn
Shive	7,104	Kg/tonne of yarn
Dust	2,824	Kg/tonne of yarn
Coarse plant residue	2,304	Kg/tonne of yarn
Direct emissions: CO_2	9,334	Kg/tonne of yarn
NH_3	68	Kg/tonne of yarn
N2O	14	Kg/tonne of yarn
NOx	6	Kg/tonne of yarn
SO_2	3	Kg/tonne of yarn
NO	2	Kg/tonne of yarn
NO_3	0.1	Kg/tonne of yarn
NMVOC	0.002	Kg/tonne of yarn

Table 11 Results of the LCA (in kg) for the production of one tonne of flax fiber yarn [53]

Scenario	GWP	AP	EP	HTP	POCP	ODP	ATP[a]
No-till and water retting	15,873	146	123	22	0.000012	0.000008	1,067
Conservation and dew retting	22,586	276	203	35	0.000026	0.000018	2,067
Conventional and bioretting	26,576	129	90	20	0.000013	0.000009	941
No-till and bioretting	26,557	129	90	20	0.000010	0.000007	942

[a] Units used in ATP are $m^3 \times 10^{12}$ per tonne of yarn

Table 12 Results of the LCA (in kg) for the production of one tonne of flax fiber sliver [53]

Scenario	GWP	AP	EP	HTP	POCP	ODP	ATP[a]
No-till and water retting	11,062	141	102	22	0.000011	0.000008	1,027
Conservation and dew retting	17,889	265	195	34	0.000025	0.000018	1,986
Conventional and bioretting	18,570	121	89	15	0.000012	0.000009	905
No-till and bioretting	18,549	121	99	15	0.000010	0.000007	905

[a] Units used in ATP are $m^3 \times 10^{12}$ per tonne of yarn

Table 13 Results of the NRADP contribution for the production of one tonne of flax fiber sliver and yarn (multiplied by 10^{15}) [53]

Scenario	Production	Oil	Coal	Gas
No-till and water retting	Yarn	1,200	5.6	3.3×10^6
	Sliver	1,100	1.8	1.0×10^6
Conservation and dew retting	Yarn	2,600	6.2	3.6×10^6
	Sliver	2,500	2.3	1.3×10^6
Conventional and bioretting	Yarn	1,500	17	9.9×10^6
	Sliver	1,400	13	7.3×10^6
No-till and bioretting	Yarn	1,200	17	9.9×10^6
	Sliver	1,100	13	7.3×10^6

was calculated for diesel and electricity usage at each stage of production of flax fibers, as shown in Table 13 [53, 61].

As compared to the other production strategies, the no-till and water retting technique of flax yarn production leads to lower impacts on global warming and eutrophication. Although the conservation tillage technique with dew retting has a lower impact on global warming as compared to conventional tillage with bioretting and no-till with bioretting, it shows the highest effects on all other types of environmental impacts owing to the use of herbicides as a desiccant in the stand/dew retting process. The bioretting process leads to a slight improvement in all impact categories except global warming potential, which is higher in the case of the bioretting process [53, 61].

5.3 LCA of Jute Fibers

A few researchers have investigated the environmental impacts of jute fiber using the LCA tool. Tables 14, 15, 16 and 17 provide the LCA results for different phases of jute yarn such as cultivation and retting phase, manufacturing phase, and product disposal phase. The results in Table 14 are for final raw jute (dried fiber), which has been produced after retting of jute plants cultivated in 1 hectare land. The results in Table 14 are obtained for 684 tonnes of jute yarn, and Tables 16 and 17 indicate the results of jute yarn disposal through incineration and landfill, respectively. This LCA study has considered the credits of jute product incineration for energy production to replace fossil fuel utilization and also considered only 50 % of methane emission and capture of the remaining 50 % during jute product disposal through landfill [62].

It can be seen from these results that the overall greenhouse gas emission effect in the cultivation and retting phase is negative. This implies that the jute planting process acts as a carbon sink. Although the emission of methane during the retting process contributes to the greenhouse gas impact, this effect is balanced by the carbon sequestration by green jute plants during their agriculture. The

Table 14 The impact factors involved during cultivation and retting phase of final raw jute fiber (dried fiber) [62]

Impact	Specification	Value	Unit
IPCC-Greenhouse effect (direct 100 years)	CO_2, CO_2 equivalent CH_4	–4502370	g.eq. CO_2
CML-Eutrophication	Phosphate ($PO_4{}^{3-}$, $HPO_4{}^{-}$, H_3PO_4, AS P) (W)	NA	g.eq. PO_4
CML-Air-acidification	Sulphur di-oxide and Nitrogen oxides	NA	g.eq. H^+

Table 15 The impact factors involved during manufacturing phase [62]

Impact	Specification	Value	Unit
IPCC-Greenhouse effect (direct 100 years)	CO_2, CO_2 equivalent CH_4	485.71	g.eq. CO_2
CML-Eutrophication	Phosphate ($PO_4{}^{3-}$, $HPO_4{}^{-}$, H_3PO_4, AS P) (W)	NA	g.eq. PO_4
CML-Air-acidification	Sulphur di-oxide and Nitrogen oxides	NA	g.eq. H^+

Table 16 The impact factors involved in disposal of jute fiber products through incineration [62]

Incineration impact	Specification	Value	Unit
IPCC-Greenhouse effect (direct 100 years)	CO_2, CO_2 equivalent CH_4	6.895	g.eq. CO_2
CML-Eutrophication	Phosphate ($PO_4{}^{3-}$, HPO_4, $H_3PO_4{}^{-}$, AS P) (W)	NA	g.eq. PO_4
CML-Air-acidification	Sulphur di-oxide and Nitrogen oxides	NA	g.eq. H^+

Table 17 The impact factors involved in disposal of jute fiber products through landfill [62]

Impact	Specification	Value	Unit
IPCC-Greenhouse effect (direct 100 years)	CO_2, CO_2 equivalent CH_4	14.124	g.eq. CO_2
CML-Eutrophication	Phosphate ($PO_4{}^{3-}$, $HPO_4{}^{-}$, H_3PO_4, AS P) (W)	NA	g.eq. PO_4
CML-Air-acidification	Sulphur di-oxide and Nitrogen oxides	0.0001104	g.eq. H^+

manufacturing phase contributes to the greenhouse gas effect due to CO_2 emissions resulting from the use of fossil-fuel–based energy generation, purchased electricity, and freight. It can be also noticed that the disposal of jute products in an unmanaged landfill leads to the greenhouse gas effect due to methane emission. However, this impact is reduced considerably when the disposal of jute products is done through incineration to produce energy for replacement of fossil-fuel–based energy.

Table 18 Input, yield, and nitrate-N emitted (all in Kg/Ha) according to good agriculture practice production scenario for hemp, wheat, and sugar beet crop produced in france [69]

	Hemp	Wheat	Sugar beet
N (ammonium nitrate)	75	130	220
P_2O_5 (triple superphosphate)	38	64	101
Potassium chloride (K_2O)	113	90	180
CaO	333	333	333
Seed for sowing	55	120	2.5
Pesticide (active ingredient)	0	2.9	3.7
Diesel	65	101	137
Natural gas (for grain drying)	0	0	0
Agricultural machinery	16.4	28.7	34.2
Grain dry matter yield	–	5,910	–
Stem/straw dry matter yield	6,720	3,870	–
Sugar/tuber dry matter yield	–	–	11,540
Followed by catch crop (%)[a]	0	50	0
Succeeding crop	Wheat	Maize	Wheat
NO_3-N emitted	40	40	40

[a] Indicates the percentage of cases for which a catch crop is assumed to be sown between harvest of the crop and sowing of the succeeding crop

In another study carried out by Saha [63] to investigate the environmental impacts of jute fiber production, input and output nutrients and their emissions to soil were estimated. According to this study, out of 1,200 kg cow dung per ha, 9.15 kg/ha N, 8.0 kg/ha P_2O_5, and 12.75 kg/ha K_2O were emitted to the soil. Also, N, P_2O_5, and K_2O emitted to the soil from urea, triple super phosphate and muriate of potash were 50, 25, and 50 %, respectively. These emitted substances have significant environmental impacts such as eutrophication, climate change, acidification, and so on.

Islam et al. [64] investigated the environmental impacts of jute fiber production in Bangladesh. This study reported that in each year the average absorption of CO_2 from the air by jute plants is 7,302.38 thousand tonnes and emission of O_2 is 5,309.91 tonnes. Also, the jute plants produce on average 956.38 thousand tonnes of leaf and 423.4 thousand tonnes of root per year and these leaves and roots mix with the soil increasing the fertility of land through emission of urea, TSP, MP, zipsam, dolomite, ferrous sulfate, magnesium sulfate, and zinc sulfate.

5.4 LCA of Hemp Fiber

LCA has been performed on hemp fiber also to investigate its impact on sustainability issues. In a study, LCA was performed on hemp fiber and its environmental impacts were compared with other major arable crops grown in France such as wheat, sugar beet, and so on. Table 18 provides the data for input, yield,

Table 19 Inputs, yield, and nitrate-N emitted (all in Kg/Ha) according to four production scenarios for hemp produced in france [68]

	Good agricultural practice	Pig slurry	Reduced tillage	Less leaching
Pig slurry		20,000	-	-
N (ammonium nitrate)	75	0	75	75
P_2O_5 (triple superphosphate)	38	0	38	38
Potassium chloride (K_2O)	113	51	113	113
CaO	333	333	333	333
Seed for Sowing	55	55	55	55
Pesticide (active ingredient)	0	0	0	0
Diesel	65	72	39	65
Agricultural machinery	16.4	18.8	11.6	16.4
Straw dry matter yield	6,720	6,720	6,720	6,720
Followed by catch crop (%)[a]	0	0	0	0
Succeeding crop	Wheat	Wheat	Wheat	Wheat
NO_3-N emitted	40	40	40	20

[a] Indicates the percentage of cases for which a catch crop is assumed to be sown between harvest of the crop and sowing of the succeeding crop

Table 20 Environmental impacts due to field production of hemp (1 ha), wheat, and sugar beet in france, according to good agricultural practice production scenario [69]

Impact category	Unit	Hemp	Wheat	Sugar beet
Eutrophication	Kg PO_4-eq.	20.5	21.9	24.1
Climate change	Kg CO_2-eq.	2,330	3,370	4,900
Acidification	Kg SO_2-eq.	9.8	16.3	24.5
Terrestrial ecotoxicity	Kg 1,4-DCB-eq.	2.3	4.0	6.7
Energy use	MJ	11,400	18,100	26,300
Land use	m^2.year	10,200	10,200	10,200

and nitrate-N emitted for these three crops according to good agricultural practice [65–68]. The environmental impacts of good agricultural practice and other scenarios are compared in Table 19.

5.4.1 Use of Inputs and Their Impacts

It can be noticed in Table 17 that hemp fiber needs lower inputs as compared to wheat and sugar beet. The highest amount of input is required for sugar beet. The environmental impacts of these crops are provided in Table 20. It is interesting to note that except for land use, the lowest impacts in all categories were observed in the case of hemp, and sugar beet shows the highest impact. An intermediate impact level is observed in the case of wheat [69].

Table 21 Contribution of the field production of 1 ha of hemp to environmental impacts in western europe for six impact categories [69]

Impact category	Unit	Annual per capita impacts	Contribution[a] (%)
Eutrophication	Kg PO_4-eq.	38.4	53.3
Climate change	Kg CO_2-eq.	14,600	15.9
Acidification	Kg SO_2-eq.	84.2	11.7
Terrestrial ecotoxicity	Kg 1,4-DCB-eq.	146	1.6
Energy use	MJ	1,54,000	7.4
Land use	m^2.year	10,100	101.4

[a] Contributions are calculated by dividing impacts for 1 ha of hemp (Table 17) by annual per capita impacts for Western Europe in 1995

5.4.2 Relative Contribution of Hemp Field Production to Overall Impacts in Western Europe

The relative contribution of hemp crop production to overall impacts in Western Europe is provided in Table 21. It can be noticed from these normalized results that hemp fiber production has a very significant contribution to land use (101 %) and eutrophication (53 %), moderated contribution to energy use (7 %), acidification (12 %), and climate change (16 %), and a minor contribution to terrestrial ecotoxicity (1.6 %) [68, 70].

5.4.3 Contribution of Emitted Substances and Resources to Impacts Associated with Crop Production

The relative contribution of emitted substances and resources to the different impact categories for field production of hemp, wheat, and sugar beet is provided in Table 22. It can be identified from the table that eutrophication was mainly caused (75–89 %) due to NO_3 for these three crops, whereas climate change was the result of mainly N_2O (56–59 %) and CO_2 (40–43 %) emissions. NH_3, SO_2, and NO_2 emissions are the main cause for acidification and emissions of Ni (66–70 %) and Cd (26–29 %) are mainly responsible for terrestrial ecotoxicity. The use of crude oil (44–46 %) and natural gas (32–36 %) has the maximum contribution to the energy use [69].

5.4.4 The Contribution of Processes to Impacts

The relative contribution of processes (production of crop inputs, production and use of diesel, and field emissions) for hemp, wheat, and sugar beet is provided in Table 23. It can be noticed that field emissions are mainly responsible (90–95 %) for eutrophication. Climate change was the result of mainly field emissions (38–41 %), N fertilizer production (25–34 %), diesel production and use (11 %),

Table 22 Contributions (in %) to different impact categories of emitted substances and resources used associated with the field production of hemp, wheat, and sugar beet [69]

Impact category	Substances/resources	Hemp	Wheat	Sugar beet
Eutrophication	NO_3	88.6	82.4	75.1
	NH_3	3.1	5.1	7.9
	PO_4	3.4	5.4	7.7
	NO_2	4.9	7.1	9.3
Climate change	N_2O	56.2	56.6	58.7
	CO_2	42.8	42.3	40.3
	CH_4	1.0	1.1	1.0
Acidification	NH_3	29.9	31.6	35.5
	SO_2	31.1	31.9	29.7
	NO_2	39.0	36.5	34.8
Terrestrial ecotoxicity	Zn	0	0	2.4
	Ni	70.2	6.5	65.7
	Pb	3.5	4.0	3.2
	Cd	26.3	28.5	28.7
Energy use	Crude oil	44.7	45.8	43.7
	Natural gas	32.7	32.1	36.4
	Uranium	11.4	10.6	9.0
	Coal	9.3	9.5	8.8
	Others	1.9	2.0	2.1

and CaO production (6–13 %). Field emissions (33–38 %), diesel production and use (22–26 %), N fertilizer production(12–14 %), P fertilizer production (11 %), and machinery production (11–13 %) cause the acidification. The energy use is mainly contributed by N-fertilizer production (28–36 %), diesel production and use (26–29 %), and machinery production (18–21 %) [69].

5.4.5 Effect of Alternative Scenarios for Hemp Production

The influence of the hemp production scenario on environmental impacts can be seen in Table 24. The use of low-cost pig slurry instead of mineral fertilizers leads to a reduction in climate change of 24 % and energy use of 32 % but an increase in eutrophication of 16 %, acidification of 140 %, and terrestrial ecotoxicity by 1,720 %. Reduced tillage is advantageous to the farmers as it causes less erosion and lowers production costs and labor requirements and this scenario leads to reduction in climate change of 6 %, acidification of 13 %, and energy use of 16 %. The amount of nitrate leached associated with arable crops can be reduced by lowering the amount of nitrate left in the soil at harvest, shortening the time period between harvest and the next crop and reducing the precipitation during this period. Agricultural practice with less leaching can help to reduce eutrophication by 43 % and climate change by 10 % [69].

In a similar study carried out by Werf et al. [71], the environmental impacts of three hemp yarn production scenarios and a flax yarn production scenario were

Table 23 The contributions (in %) to different impact categories of the processes (production of crop inputs, production and use of diesel, field emissions) making up the field production of hemp, wheat, and sugar beet [69]

Impact category		Hemp	Wheat	Sugar beet
Eutrophication	N fertilizer production	1.0	1.5	2.4
	P fertilizer production	1.1	1.7	2.5
	K fertilizer production	0.1	0.1	0.1
	CaO production	0.2	0.2	0.2
	Pesticide production	0	0.1	0
	Machinery production	0.2	0.4	0.4
	Diesel production and use	2.7	4.0	4.9
	Field emissions[a]	94.7	92.0	89.5
Climate change	N fertilizer production	24.6	29.5	34.4
	P fertilizer production	2.8	3.3	3.5
	K fertilizer production	2.6	1.4	1.9
	CaO production	13.1	9.0	6.2
	Pesticide production	0	0.6	0.5
	Machinery production	5.3	6.4	5.3
	Diesel production and use	10.5	11.3	10.5
	Field emissions[a]	41.1	38.5	37.7
Acidifications (kg SO_2-eq.)	N fertilizer production	11.8	12.4	14.0
	P fertilizer production	10.7	10.8	11.3
	K fertilizer production	2.2	1.1	1.4
	CaO production	3.3	2.0	1.3
	Pesticide production	0	1.7	1.4
	Machinery production	12.5	13.3	10.5
	Diesel production and use	26.2	24.4	22.1
	Field emissions[a]	33.3	34.3	38.0
Energy use (MJ)	N fertilizer production	28.1	30.7	35.4
	P fertilizer production	5.6	6.0	6.5
	K fertilizer production	9.8	4.9	6.8
	CaO production	8.5	5.3	3.6
	Pesticide production	0	4.2	3.7
	Machinery production	19.3	21.2	17.5
	Diesel production and use	28.7	27.7	26.0

[a] All field emissions, except for those resulting from the field use of diesel, which is counted in 'Diesel production and use'

Table 24 Environmental impacts due to field production (1 ha) of hemp according to four production scenarios [69]

Impact category	Unit	Good agricultural practice	Pig slurry	Reduced tillage	Less leaching
Eutrophication	kg PO_4-eq.	20.5	23.7	20.2	11.6
Climate change	kg CO_2-eq.	2,330	1,770	2,200	2,090
Acidification	kg SO_2-eq.	9.8	23.5	8.5	9.8
Terrestrial ecotoxicity	kg 1,4-DCB-eq.	2.3	41.9	2.3	2.3
Energy use	MJ	11,400	7,760	9,520	11,400
Land use	m^2.year	10,200	10,200	10,200	10,200

Table 25 Environmental impacts of yarn production expressed per 100 kg of yarn for the investigated scenarios: Hemp Water Retting (HW), Hemp Bioretting (HB), Baby Hemp (BH), and Flax Dew Retting (FD) [70]

Impact category	Hemp			FD
	HW	HB	BH	
Eutrophication (kg PO_4-eq.)	3.04	3.02	4.94	2.61
Climate change (kg CO_2-eq.)	1350	1810	1460	1360
Acidification (kg SO_2-eq.)	7.38	9.01	8.02	8.16
Nonrenewable energy use (MJ)	25,500	35,800	26,500	26,100
Land occupation (m^2 year)	1,160	1,260	2,410	1,150
Pesticide use (act. subst.) (kg)	0	0	0.874	0.296
Water use (m^3)	19.9	22.1	7.63	7.23

Table 26 Normalized impacts (i.e., contribution of production of 100 kg of yarn according to the investigated scenarios (Hemp Water Retting (HW), Hemp Bioretting (HB), Baby Hemp (BH), and Flax Dew Retting (FD))) to per capita environmental impacts in Western Europe [70]

Impact category	Normalization value	Contribution (%)			
		HW	HB	BH	FD
Eutrophication (kg PO_4-eq.)	38.4	7.9	7.9	12.9	6.8
Climate change (kg CO_2-eq.)	14,600	9.2	12.4	10.0	9.3
Acidification (kg SO_2-eq.)	84.2	8.8	10.7	9.5	9.7
Nonrenewable energy use (MJ)	154,000	16.6	23.2	17.2	16.9
Land occupation (m^2 year)	10,100	11.5	12.5	23.9	11.4

compared through LCA. The traditional warm-water retting-based hemp processing was compared with bioretting (hemp green scutching followed by water retting), baby hemp (based on stand retting of premature hemp), and dew retting of flax. Table 25 lists the impacts for production of 100 kg yarn in these four scenarios. It can be observed that none of the alternative scenarios seem better in all aspects as compared to the conventional warm-water retting-based processing. The dew retting of flax has similar environmental impacts as the conventional hemp production scenario. However, the conventional hemp production scenario consumes more water than the flax production scenario which, however, uses more pesticides. The relative contribution of the production of 100 kg of yarn to per capita environmental impacts in Europe is provided in Table 26. It is clear from the table that the environmental impacts resulting from hemp fiber production can be reduced through reduction of energy use in the fiber processing and yarn production stages and also by reducing eutrophication in the crop production phase. Moreover, the impacts per kg of final product can be reduced by increasing the yield in every processing step without increasing the inputs. In particular, the long fiber yield, which is currently less than 30 %, should be increased through the optimization of processing steps. Also, looking at the labor costs in Europe, hemp bioretting may prove to be a useful production scenario that involves a low labor requirement and provides a satisfactory environmental profile.

6 Conclusions

This chapter presents production, properties, applications, and sustainability aspects of some important natural plant fibers such as cotton, flax, hemp, and jute. Due to good comfort characteristics, cotton fiber is mainly used in the apparel sector. Studies revealed that production of cotton fabrics requires significantly less energy and natural resources such as oil and gas, as compared to polyester fabrics. However, cultivation of cotton fiber needs chemical fertilizers and more water and leads to emission of higher amounts of carbon dioxide and sulfur dioxide than polyester fibers. Moreover, cotton fiber cultivation can affect the soil due to land preparation leading to soil erosion. However, modern technologies of cotton cultivation using conservation tillage avoid mixing and disturbing the soil to a much lesser extent and thereby prevent soil erosion. Also, cotton is being cultivated nowadays using much smaller amount of insecticides and pesticides and also using less land. The production of organic cotton does not use pesticides and synthetic fertilizers and therefore has much lower environmental impacts as compared to conventional cotton. The production of biofuel from cotton seeds is a modern strategy to balance the energy requirements of cotton fiber. Jute fiber is a type of bast fiber that finds widespread applications in home textiles, building materials, structural composites, automotive and protective textiles, and so on. Jute fiber is considered sustainable due to the fact that it is produced from a renewable resource with very high biomass production rate per unit land area, can be produced without using chemical fertilizers; jute planting leads to enrichment of the soil and the CO_2 assimilation rate of jute is several times higher than that of other trees. The main environmental concern related to jute production is the generation of methane gas during the retting process and this can be significantly suppressed using modern retting techniques such as ribbon retting, humidified retting, and so on. Antiallergic characteristics, good moisture absorbency, and breathability as well as good mechanical properties make flax or linen fibers popular for bed and bath fabrics such as tablecloths, dish towels, bed sheets, and the like; home and commercial furnishing items (wallpaper/wall coverings, upholstery, window treatments, etc.); apparel items (suits, dresses, skirts, shirts, etc.); and industrial products (luggage, canvases, sewing thread, etc.). Sustainability of linen fibers can be significantly improved using minimal or shallower plowing which reduces energy requirements and soil erosion considerably as well as using no-till and warm-water retting to reduce the environmental impact potentials. Moreover, the use of warm-water retting can reduce the energy requirement significantly. The use of coproducts such as short fiber and shives in animal bedding or in paper production and use of dusts produced from the scutching and hackling process as biomass fuel can also add to the sustainability of linen fibers. Hemp fiber also finds several applications in apparel, furnishings, and industrial textiles and its production can be considered to be sustainable. The factors responsible for sustainability of hemp fibers are the use of very less amount (or no) pesticides during hemp cultivation, enrichment of soils and reduction of soil erosion, soil purification, very high production rate, and absorption of CO_2, among others.

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Natural Dyes: Sources, Chemistry, Application and Sustainability Issues

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Abstract Dyes derived from natural materials such as plant leaves, roots, bark, insect secretions, and minerals were the only dyes available to mankind for the coloring of textiles until the discovery of the first synthetic dye in 1856. Rapid research strides in synthetic chemistry supported by the industrialization of textile production not only led to the development of synthetic alternatives to popular natural dyes but also to a number of synthetic dyes in various hues and colors that gradually pushed the natural dyes into oblivion However, environmental issues in the production and application of synthetic dyes once again revived consumer interest in natural dyes during the last decades of the twentieth century. Textiles colored with natural dyes are preferred by environmentally conscious consumers and today there is a niche market for such textiles. But the total share of natural dyes in the textile sector is approximately only 1 % due to certain technical and sustainability issues involved in the production and application of these dyes such as nonavailability in ready-to-use standard form, unsuitability for machine use, and limited and nonreproducible shades. Natural dyes per se are sustainable as they are renewable and biodegradable but they cannot fulfill the huge demand from the textile sector in view of the preferential use of land for food and feed purposes. Also, overexploitation of natural resources to obtain dyes may result in deforestation and threaten endangered species. For these reasons, the Global Organic Textiles Standard (GOTS) permits the use of safe synthetic dyes and prohibits the use of natural dyes from endangered species. Various research efforts have been undertaken all over the world to address the shortcomings of natural dyes in view of the tremendous environmental advantage they offer. This book attempts to review the current status of natural dyes and various sustainability issues involved in their production and application and examines their future prospects.

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1 Introduction

The art of dyeing is as old as our civilization. Dyed textile remnants found during archaeological excavations at different places all over the world provide evidence to the practice of dyeing in ancient civilizations. Natural dyes were used only for coloring of textiles from ancient times till the nineteenth century. As the name suggests, natural dyes are derived from natural resources. Coloring materials obtained from natural resources of plant, animal, mineral, and microbial origins were used for coloration of various textile materials. Different regions of the world had their own natural dyeing traditions utilizing the natural resources available in that region. Use of natural dyes started to decline after the invention of synthetic dyes in the second half of the nineteenth century. Concerted research efforts in the field of synthetic dyes and rapid industrialization of textile production resulted in almost complete replacement of natural dyes by synthetic dyes on account of their easy availability in ready-to-apply form, simple application process, consistency of shades, and better fastness properties. The tradition of using natural dyes could survive only in certain isolated pockets. Recent environmental awareness has again revived interest in natural dyes mainly among environmentally conscious people. Natural dyes are considered eco-friendly as these are renewable and biodegradable; are skin friendly and may also provide health benefits to the wearer. Natural dyes can be used for dyeing almost all types of natural fibers. Recent research shows that they can also be used to dye some synthetic fibers. Apart from their application in textiles, natural dyes are also used in the coloration of food, medicines, handicraft items and toys, and in leather processing, and many of the dye-yielding plants are used as medicines in various traditional medicinal systems. There are several challenges and limitations associated with the use of natural dyes. The current dyestuff requirement from the industry is about 3 million tonnes. Considering this fact, the use of natural dyes in mainstream textile processing is a big challenge. As agricultural land is primarily required to feed an ever-increasing world population and support livestock. and biodiversity should not be compromised for the extraction of dyes, sustainability of natural dyes is a major issue. This chapter discusses various issues related to the use of natural dyes in textiles such as potential sources, chemistry, extraction methods, application methods, and sustainability issues.

2 Potential Sources of Natural Dyes

Natural dyes are derived from natural resources and based upon their source of origin, these are broadly classified as plant, animal, mineral, and microbial dyes although plants are the major sources of natural dyes. As interest in natural dyes grew, information from the old literature was collected and traditional dyeing practices in different regions were documented and compiled by various researchers. Adrosko [1] published a book on natural dye sources and processes for their application to textiles at the household level. DOBAG, the Turkish acronym for Natural Dye Research and Development Project, launched in Turkey with German assistance in cooperation with Marmara University, Istanbul in 1981 was a big success in reviving the lost art of producing naturally dyed carpets. Natural dyeing processes of India were documented in a book by Mohanty et al. [32]. Chandramouli [9] also published a book on natural dyeing processes of India. Dyes traditionally used in the Scottish Highlands were reviewed by Grierson et al. [15]. Buchanan [8] presented a detailed account of dye plants used for natural dyeing of textiles such as alkanet, annatto, chamomile, coreopsis, madder, safflower, indigo, and so on, and methods for dyeing of textiles with these. Later information on various dye-yielding plants, methods to grow them, harvesting dye parts, methods to dye wool and silk with them, and color shades obtained were also detailed by her [7]. Research efforts by individuals and organizations and exchange of available information through various seminars, symposiums, workshops, and research articles have now revealed various natural dye sources. Plenty of information about different sources of natural dyes is now available in the literature [54, 55]. A brief account of the potential dye resources according to their source of origin is listed below.

2.1 *Plant Origin*

Historically, plants have been used for the extraction of a majority of natural dyes. Various plant parts including roots, leaves, twigs, stems, heartwood, bark, wood shavings, flowers, fruits, rinds, hulls, husks, and the like serve as natural dye sources. The famous natural blue dye, indigo is obtained from the leaves of the plant *indigofera tinctoria.* Some plant-derived dyes have other applications also, for example, as food ingredients and medicines in traditional medicine systems and hence a commercial supply chain of these dyes is in place. Some of the natural dyes were well known in the past for their dyeing properties and have remained in use even now, albeit on a small scale. A renewed interest in natural dyes has increased their commercial availability. Some such important dyes reported in many publications [6, 19, 26] are listed below.

2.2 *Blue Dyes*

Indigo is the only important natural blue dye. Leaves of the plant *indigofera tinctoria* are the best source of this dye. This very important dye popularly known as the “king of natural dyes” has been used from ancient times till now for producing blue color and is today most popular for denim fabrics. The coloring matter is present in indigo plant leaves as a light yellow substance called indican

(1H-indol-3yl β-D-glucoside). The leaf production from one acre of cultivated indigo plants is approximately 5,000 kg which can yield about 50 kg of pure natural indigo powder after processing. It is produced by fermenting the fresh plant leaves, and cakes thus prepared are used for dyeing purposes. Apart from *indigofera* species, there are several plants that can be used to produce indigo dye. Woad is a natural indigo-producing plant in Europe. Apart from this, dyers knotweed (*Polygonum tinctorium*) and Pala Indigo (*Wrightia tinctoria*) are some of the plants used to produce indigo traditionally. The use of natural indigo started declining after the manufacture of synthetic indigo by BASF in 1987.

2.3 Red Dyes

There are several plant sources of red natural dyes. A few popular sources are listed below.

2.4 Madder

Madder is the red color producing natural dyes from the plants of various *Rubia* species. The dye is obtained from the roots of the plant. It is also popularly known as the "queen of natural dyes." The main coloring constituent of European madder *Rubia tinctorum* is alizarin. The yield of roots from the 3-year-old plant is between 3–5 tonnes per hectare and about 150–200 kg of dye. As with indigo, the use of natural madder powder started declining after the manufacture of synthetic alizarin by the BASF. *Rubia cordifolia* is known as Indian madder, manjishth, or manjeet, and its coloring matter is a mixture of munjistin and purpurin. In addition to roots, dye is also present in the stems and other parts of the plant.

Dye is usually extracted by boiling dried root chips or stem pieces with water but sometimes, these are merely steeped in cold water for few hours. As it is a mordant dye, it produces brightly colored insoluble complexes or lakes with metal ions present on the mordanted fabric. Alum is widely used to get pink and red shades. A mixture of alum and iron produces purple shades. Alum can be used as a primary metallic salt in combination with other mordants to develop a range of red shades. Dyed materials possess good fastness properties.

2.5 Brazil Wood/Sappan Wood

A red dye is obtained from the wood of *Caesalpina sappan*, a small tree found in India, Malaysia, and the Philippines which is known as sappan wood or "Patang." The same dye is also present in Brazil wood (*Caesalpinia echinata)*, the name being derived from the word braza meaning glowing like fire due to the bright red color of its wood. Aqueous extraction can be used to extract the dye. Alkali extraction deepens the red color. Textile materials can be dyed to get the red color with or without the use of alum mordant. A combination of this dye with turmeric produces orange shades and a deep maroon color is produced with catechu.

2.6 Morinda

The root and bark of the tree *Morinda citrifolia* growing in India and Sri Lanka is used for getting red shades. Maximum coloring matter can be obtained from the 3 to 4-year-old tree. Mature trees have very little dye. Dye is extracted from the chipped material with water after a preliminary wash to remove free acids. Various shades including purple and chocolate can be produced with the use of mordants.

2.7 Safflower

Safflower is an annual herb known to have originated in Afghanistan. It is mainly cultivated for oil from its seeds which are rich in polyunsaturated fatty acids. The safflower florets were traditionally used for extracting dye which was valued for its bright cherry-red color. It contains two coloring matters, a water-soluble yellow present in abundance (26–36 %) which was not used as a dye and the scarlet red water-insoluble carthamin present only to the extent of 0.3–0.6 %. The yellow amorphous coloring matter has to be completely removed from carthamin before the latter is used for dyeing as its presence even in small quantities affects the pure pinkish shade imparted by the red dye. Safflower has been employed to give cherry-red direct dyeings on silk and cotton. The dye is extracted from dried safflower florets by continuously washing it with acidulated water to remove all the water-soluble yellow coloring matter. The residue containing insoluble red dye is either dried partially and molded into cakes for use in dyeing or it is extracted with a sodium carbonate solution and precipitated by dilute acids. The washing and light fastness of the dye is poor. Yellow dye has now also been used to dye mordanted cotton.

2.8 Yellow Dyes

Yellow dyes are available from several plant resources. Some of the prominent sources are listed below.

2.9 Turmeric

Turmeric is a well-known natural dye. The dye is extracted from the fresh or dried rhizomes of turmeric. The dye present is chemically curcumin belonging to the Diaroylmethane class. It is a substantive dye capable of directly dyeing silk, wool, and cotton. The shade produced is fast to washing but its fastness to light is poor. The natural mordants such as tannin obtained from myrobolan can be used to improve the fastness properties. Turmeric dyeings can be overdyed with indigo for production of fast greens.

2.10 Saffron

Saffron is an ancient yellow dye belonging to the family Iridaceae and is obtained from the dried stigmas of the plant *Crocus sativus*. It is grown in the Mediterranean, Iran, and India, and used for cooking as well as medicinal purposes. The dye is extracted from the stigmas of flowers by boiling them in water. It imparts a bright yellow color to the materials. It can directly dye wool, silk, and cotton. Alum mordant produces an orange yellow known as saffron yellow.

2.11 Annatto

Annatto *Bixa orellana* is a small tree belonging to the family Bixaceae. The tree is known for the yellow orange dye obtained from its seeds. It is extensively used for the dyeing of cotton, wool, and silk and also used for coloring butter, cheese, and the like. The pulp is rich in tannin. The alkali extraction method is used for extracting dye at boiling conditions. It produces reddish orange shades on cotton, wool, and silk.

2.12 Barberry

The barberry *(Berberis aristata)* plant roots, bark, and stems are used to extract the dye. The main constituent of the dye is berberine which is an alkaloid. It is a basic dye and can be used to dye silk and wool directly. The dye produces a bright yellow color with good washing fastness and average light fastness. Cotton can be dyed after mordanting.

2.13 Pomegranate

Rinds of pomegranate (*Punica granatum*) fruits are rich in tannins and are used for mordanting purposes. A yellow dye is also present which can be used to dye wool, silk, and cotton with good fastness properties. It is also used along with turmeric for improving the light fastness of the dyed materials.

2.14 Myrobolan

Dried myrobolan (*Terminalia chebula*) fruits have high tannin content and also contain a natural dye that is used for producing bright yellow shades for all textile materials. Myrobolan is also used as a natural mordant to fix different natural dyes on textile materials. Myrobolan is a part of the famous Ayurvedic preparation "triphala" and dyed materials are also imparted with medicinal properties such as antimicrobial, antifungal, and so on.

2.15 Marigold

Marigold (*Tagetus spp.*) is a bright yellow flower-yielding plant. It is commonly used for making garlands and floral decorations. It is available in different colors including yellow, golden yellow, orange, and the like. The main coloring component is quercetagetol, a flavonol along with two of its glycosides and lutein. It dyes wool and silk in deep yellow colors with good fastness properties. Cotton can be dyed with this dye in combination with mordants to get fast colors. Cotton fabrics are pretreated with tannic acid/tannin-containing mordants followed by metallic mordants before dyeing to get various shades.

2.16 Flame of the Forest

The flame of the forest (*Butea monosperma*) tree, locally known as tesu in India, produces bright orange color flowers. The dye extracted from the flowers can be used for dyeing all natural fibers. Bright yellow to brown and orange colors can be produced with suitable mordant.

2.17 Kamala

The dried fruit capsules of kamala (*Mallotus phillipensis*) yield a red-orange powder that can be used for dyeing wool and silk to bright orange-yellow and golden-yellow colors. Colors produced on cotton are not so good with moderate fastness properties.

2.18 Onion

The outer skin of onion (*Allium cepa*) which is generally thrown away as waste can be used to extract yellow color natural dye. The dye is flavonoid in chemical constitution, and produces bright colors on wool and silk. Cotton can be dyed with suitable mordant. The washing and light fastness of the shade produced are moderate.

2.19 Weld

Weld (*Reseda luteola*) was a very important yellow dye plant in Europe. The coloring matter is a flavonoid and it produces a good yellow color on natural fiber textiles that have very good fastness properties.

2.20 Dolu

Roots and rhizomes of Himalayan rhubarb *(Rheum emodi*) yield a yellow dye that can be used to dye wool, silk, and cotton after mordanting with exceptional fastness properties.

2.21 Brown and Black Dyes

Oak galls are rich in tannin and are used for mordanting. They can also be used to get a brown color. Catechu or cutch obtained from the heartwood of *Acacia catechu* is used to dye cotton, wool, and silk to brown color directly. It is also rich in tannins and can be used to get black color with iron mordant. Black color can also be obtained from many yellow and red dyes by iron mordanting. Famous logwood black color having very good fastness properties was obtained by using iron mordant and the extract of logwood obtained from the heartwood of the tree *Haematoxylon campechianum* found in Mexico and the West Indies.

Apart from the above-mentioned sources, there have been efforts by various researchers to explore local flora for their potential to dye textiles. Leaves, flowers, wood, bark, and so on of several plant materials have been utilized for the dyeing of various textile substrates with varying results in terms of deepness of color produced on the substrates and their colorfastness properties. Every year new additions are being made to the list of plant species that can be used as dye sources. Some of the promising natural dyes reported in the literature [20, 21, 33, 35, 45, 57] are given in Table 1.

In an UNDP-sponsored project executed in India, the potential of about 120 plant materials from the Western Ghats of India, a biodiversity-rich region was

Table 1 Some promising natural dye sources

S.No	Common name of the plant	Botanical name	Part used	Color obtained
1	Siam weeds	*Eupatorium odoratum*	Whole plant	Yellow
2	Goat weed	*Ageratum conyzoides*	Whole plant	Yellow
3	Jack fruit tree	*Atrocarpus heterophyllus*	Bark	Yellow
4	Gulmohar	*Delonix regia*	Flower	Olive green
5	Teak	*Tectona grandis*	Leaves	Yellow
6	Babool	*Acacia nilotica*	Leaves, bark	Yellow/brown
7	Water lilly	*Nymphaea alba*	Rhizomes	Blue
8	Dahlia	*Dahlia variabilis*	Flowers	Orange
9	Amla	*Emblica officinalis*	Bark, fruit	Grey
10	Indian Jujube Ber	*Ziziphus mauritiana*	Leaf	Pink
11	Drumstick	*Moringa pterygosperma*	Leaf	Yellow
12	Sausage tree	*Kigelia pinnata*	Petals, heartwood, bark	Yellow, pink
13	African tulip tree	*Spathodeacompanulata*	Flower	Yellow/orange
14	Tamarind	*Tamarindus indica*	Leaves, seeds	Yellow, brown
15	Golden dock	*Rumex maritmus*	Seeds	Brown
16	Eucalyptus	*Eucalyptus camaldulensis*	Bark	Yellow and brown
17	Red sandalwood	*Pterocarpus santalinus*	Wood	Red

explored for the dyeing of cotton. Based on the color produced and colorfastness of dyed material to light and washing, more than a hundred of these were found to be promising [3].

2.22 Animal Origin

Insects were the main source of natural dyes of animal origin and most of these provided red colors. The oldest animal origin dye, Tyrian purple, produced from the secretions of the sea mollusc *Murex* is an exception. This dye produced a very fast deep violet color on fabrics. It was very expensive as thousands of molluscs were needed to get a gram of the dye. Hence it was considered a symbol of royalty and was used to color the clothes of the royal family. Cochineal was an important animal origin dye obtained from the insects of the species called *Dactylopius coccus* which is still being used to dye textiles. The dye is obtained from the bodies of female insects that live on cactus (*Opuntia* species). The principal coloring matter is carminic acid. The cochineal dye produces crimson red color on animal fibers and has good washing and light fastness properties. Its bright red aluminum calcium chelate known as carmine is used as food color. Kermes is another animal origin crimson red dye derived from the insect *Kermes licis.* This dye has been known since ancient times to color animal fibers but was inferior to cochineal in fastness properties. Lac was also well known in ancient times for coloration of animal fibers. It is obtained from the hardened secretions (stick lac) of the insect *Kerria lacca* found on the twigs of certain tree varieties in India and the SouthEast Asia region. It is obtained as a by-product during the processing of stick lac for obtaining shellac. Traditionally, it was used for coloration of animal fibers only as it had good affinity for those but it has now also been used by many researchers [44, 48] to color cellulosic fibers such as cotton as it is available in fairly large quantities as a by-product. Recently the kinetics for the dyeing of cotton with this dye has been studied by Chairat et al. [10].

2.23 Mineral Origin

Some mineral pigments found in nature such as cinnabar, red ocher, yellow ocher, raw sienna, malachite, ultramarine blue, azurite, gypsum, talc, charcoal black, and so on, have been used for coloration purposes. Apart from the red ocher that was used by the monks for coloration of their robes, these were mainly used in paintings and murals along with gum as binder. Extensive details of the natural mineral pigments used in India have been provided by Agarwal and Tiwari [2]

2.24 Microbial and Fungal Origin

Some bacteria produce colored substances as secondary metabolites. *Bacillus, Brevibacterium, Flavobacterium, Achromobacter*, *Pseudomonas, Rhodococcus spp.* are some of the pigment-producing bacteria [27]. Some bacteria have also been reported to produce indigo upon exposure to petroleum products. A list of pigment-producing microorganisms and chemical classes of pigments produced by them has been provided in a review by Malik et al. [30].

Microbes as a dye source offer an advantage as these can be easily grown on cheap substrates under controlled conditions. The dyeing of nylon with prodigiosin pigment extracted from *Serratia marcescens* was attempted by Vigneswaran et al. [56]. They investigated the growing conditions of the *Serratia* strain for pigment production and its extraction. Extracted pigment was characterized and its heat stability and dyeing characteristics for various textile substrates were studied. Pink coloration obtained on wool was fast to washing but its very poor fastness to light did not encourage future work for use as textile dye.

Pigments from the fungus *Monascus purpureus* are used for coloration of some traditional oriental food items. It has been used for fabric coloration also. *Trichoderma* sp. has been used for coloration of silk and wool with excellent washing fastness [17].

Lichens and mushrooms have been used as sources of colorants in Europe and in some other parts of the world. Orchil dye from lichens was used to create violet and purple shades as a cheap alternative to costly purple dye from molluscs. They have also been used to dye wool to shades of yellow, brown, and reddish brown. Orchil and litmus colorants obtained from lichens are not found in higher plants.

Dyes derived from mushrooms have become popular since the 1970s. Some *Cortinarius* species have intensely colored fruiting bodies and are the best mushroom dyes. *Cortinarius sanguineus* (blood-red webcap) contains anthraquinone pigments emodin and dermocybin in glucoside form. The dye content is about 6 % and a preparative scale extraction process has been described by Hynninen et al. [24]. These pigments were used by Raisanen et al. [40, 41] to dye both natural and synthetic fibers with low to excellent fastness properties. A list of pigments present in various lichens and fungi along with their chemical structures has been compiled by Raisanen [42] and a very elaborate account of different lichens and mushroom types consisting of their description, habitat, distribution, harvesting procedures, dye composition, dyeing methods, color obtained, historical importance, other uses, and possible future developments has been presented by Cardon (2007).

3 Chemistry and CI Numbers

As dyes have complex chemical structures, their chemical names are difficult to understand and remember and common names are in the local languages and are area specific, a color index has been developed for identifying the dyes. It serves as reference for both the chemical and technical properties of dyes. Earlier published by the Society of Dyers and Colorists (SDC), United Kingdom, it is now jointly published by SDC and the American Association of Textile Chemists and Colorists (AATCC), United States. In the color index, dyes are classified according to major application classes. Within the application class, the dyes are arranged according to the hue. Dyes whose chemical structures are known are also given a constitution number that denotes their chemical constitution. Thus a dye has a CI constitution number assigned to its chemical constitution and also a name in the color index which denotes the type of dye. For example, the CI number of natural indigo dye is 75780 with the name CI Natural Blue 1 in which CI denotes Color Index, Natural indicates type of dye, Blue indicates the hue, and 1 is the identifying number. Natural dyes have been grouped together as a class in the color index. In Volume 3 of the color index, 32 natural reds, 6 natural oranges, 3 natural blues, 5 natural greens, 29 natural yellows, 12 natural browns, 6 natural blacks, and 1 natural white have been listed.

Natural dyes have a complex chemical constitution. Unlike synthetic dyes, they are usually not a single entity but a mixture of closely related chemical compounds. On the basis of major chemical constituents present, they are divided into:

1. Indigoid dyes
2. Anthraquinone dyes
3. Naphthoquinone, Benzoquinone dyes
4. Flavonoid dyes
5. Carotenoid dyes
6. Tannin-based dyes.

3.1 Indigoid Dyes

Indigo is the major and most important dye in this class as among natural dyes, it is almost always the source of the primary color blue. Chemically it is indigotin (C.I. Natural Blue1, C.I. 75780) and is found in largest concentration in the leaves of some Indigofera species such as *I. tinctoria, I. errecta*, and *I. sumatrana*, among others. It is also the coloring matter of pala indigo (*Wrightia tinctoria*), Assam indigo (*Strobilanthes flaccidifolius*), and woad (*Isatis tinctoria*); the last one was used in Europe for blue color before being replaced by superior indigo from India. Indigo is not soluble in water and has to be reduced to its water-soluble leuco form through a reduction process. This water-soluble form of indigo is used for dyeing textiles. After dyeing, the leuco form is oxidized by atmospheric air to its original blue indigotin structure. It has excellent colorfastness properties. It is similar in structure to synthetic indigo (C. I. Vat Blue1, C.I. 73000) but it also contains some amount of red dye indirubin which imparts a rich reddish tone to the textiles dyed with natural indigo.

Tyrian purple obtained from Mediterranean molluscs of the *Purpura* and *Murex* genus is another indigoid dye that also has excellent fastness properties. Chemically, it is the 6, 6' dibromo derivative of indigo (Fig. 1).

3.2 Anthraquinone Dyes

The basic chemical structure of anthraquinone is depicted in Fig. 2. A large number of natural dyes especially red color-producing dyes fall into this category. The most famous natural dye in this category is alizarin obtained from European madder (Rubia tinctorum). Other dyes include lac, cochineal, morinda, and Indian madder (manjishth/manjeet) among others. The chemical names, CI numbers, and names of some anthraquinone dyes and their sources are given in Table 2.

Carthamin from safflower (*Carthamus tinctorius*) florets is an old traditional red dye having a benzoquinone structure. It gives cherry red and pink shades on silk and cotton but fastness properties are not good.

3.3 Naphthoquinone Dyes

The basic structure of the Naphthoquinone is depicted in Fig. 3. Some of the natural dyes belonging to this category are henna, walnut shells, and so on. The coloring matter of henna is lawsone which is 2-hydroxy naphthoquinone and walnut shells contain juglone which is 5-hydroxy naphthoquinone. These dyes also produce orange, red, or reddish brown shades like anthraquinone dyes (Fig. 4 and Table 3).

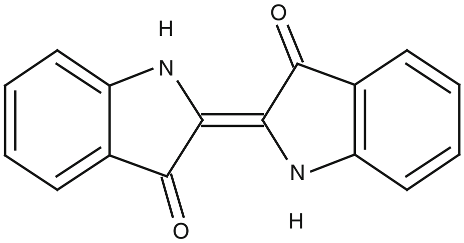

Fig. 1 Indigotin

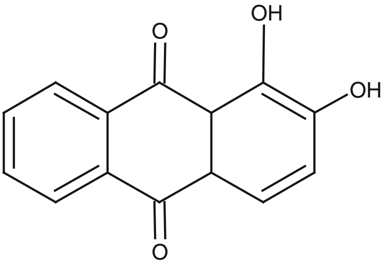

Fig. 2 Alizarin (1, 2-dihydroxy anthraquinone)

Table 2 Some anthraquinone dyes [14]

Dye name	CI number	CI name	Natural sources
Alizarin	75330	Natural red 6, 8, 9, 10, 11, 12	Madder, chayroot
Purpuroxanthin or xanthopurpurin	75340	Natural red 8, 16	Madder, munjeet
Morindadiol	75380	Natural red 18	Morinda root
Soranjidiol	75390	Natural red 18	Morinda root
Purpurin	75410	Natural red 16, 8	Munjeet, madder
Pseudopurpurin	75420	Natural red 14, 9, 8	Gallium, madder
Laccaic acid	75450	Natural red 25	*Coccus laccae* (Lac dye)
Kermesic acid	75460	Natural red 3	*K. licis*
Carminic acid or cochineal	75470	Natural red 4	*C. cacti*

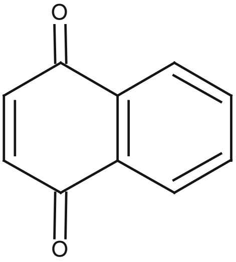

Fig. 3 Naphthoquinone

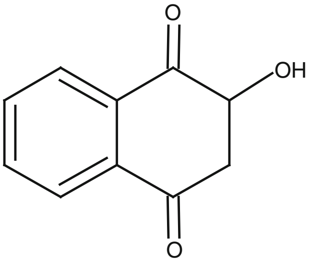

Fig. 4 Lawsone

Table 3 Some naphthoquinone dyes [14]

Dye name	CI number	CI name	Natural sources
Lawsone	75480	Natural orange 6	Henna
Lapachol	75490	Natural yellow 16	Taigu or lapachol wood
Juglone	75500	Natural brown 7	Walnut shells
Alkanan	75520	Natural red 20	Ratanjot, *Anchusa tinctoria*

3.4 Flavonoid Dyes

Most of the yellow natural dyes have an hydroxyl or methoxy substituted flavone structure. Dyes with this chemical constitution are found in a wide variety of natural resources. Weld (*Reseda luteola*) or dyer's rocket was widely used in Europe to produce fast and brilliant colors on wool and silk. The coloring matter present is flavone luteolin (CI Natural yellow 2) and its structure is given in Fig. 5. Marigold (*Tagetus* spp.) flowers contain a flavonol dye quercetagetol. Some other flavonoid dyes are listed in Table 4.

Dihydropyrans are closely related to flavones in structure. Haematin and its leuco form haematoxylin, which are the main coloring substances present in Logwood (heartwood of *Haematoxylon campechianum*, CI natural black 1), belong to this category. Dye from the wood of *Caesalpinia echinata* (Brazil wood) and *Caesalpinia sappan* (Sappan wood) also belongs to this group. The coloring matter present in both is brazilin which gets oxidized to the red-colored compound brazeilein.

Butein, a yellow-orange dye from *Butea monosperma* (tesu) flowers, and rottlerin, the main coloring matter of orange red powder from ripe fruit capsules of *Mallotus phillipensis* (Kamala) (CI Natural orange 2) which produces a yellow color, have chalcone structures which can be considered as open chain analogues of flavonoids (Fig. 6).

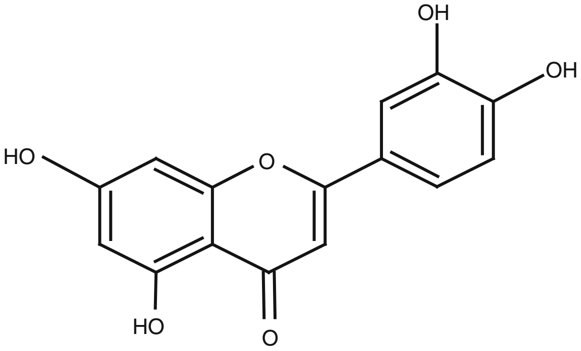

Fig. 5 Luteolin

Table 4 Some flavonoid dyes [14]

Dye name	CI number	CI name	Natural sources
Luteolin	75590	Natural yellow 2	Dyers rocket, dyers wood,
Kaempferol, trifolitin or indigo yellow	75640	Natural yellow 13,10	Natal indigo, saffron
Kaempferol 7-methyl ether	75650	Natural green 2, natural yellow 13	Sap green, Hungarian berries
Quercetin, meletin or sophoretin	75670	Natural yellow 10, Natural red I	Persian berries, toon or Indian mahogany tree
Quercitrin	75730	Natural yellow 10	Quercitron bark
Rutin	75740	Natural yellow 10	Chinese or Avignon berries

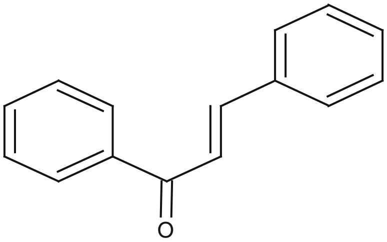

Fig. 6 Chalcone

3.5 Carotenoid Dyes

The major dyes in this class are bixin and nor bixin found in annatto seeds and crocin found in saffron stigma (CI Natural orange 4). Orange dye from the corolla tubes of *Nyctanthes arbor-tristis* flowers or nictanthin also has a similar carotenoid structure (Fig. 7).

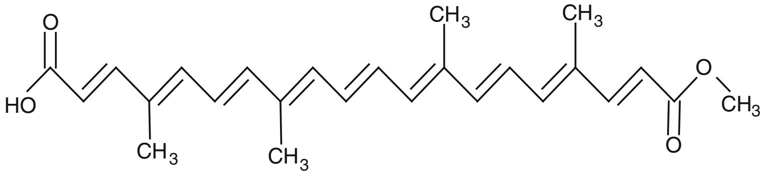

Fig. 7 Bixin

3.6 Tannin-Based Dyes

Tannins are polyphenolic compounds that are present in many natural resources used for dyeing purposes. The dyes with tannin generally require mordants for fixing onto the fabric. This class of dyes also tends to change color with the change in mordant depending upon the dye-mordant complex. Dye obtained from the bark of *Acacia nilotica* (Babool; CI Natural Brown 3) and wood of *Acacia catechu* (Cutch) have a polyphenolic structure.

3.7 Others

Curcumin, the yellow coloring matter of turmeric, a well-known spice and food color, belongs to the diaroyl methane class. Berberine present in *Berberis aristata* and *B. vulgaris* root and stems and bark of the Amur cork tree (*Phellodendron amurens)* belongs to the alkaloid category and is the only known basic natural dye.

4 Production Techniques for Natural Dyes

Unlike synthetic dyes, which are synthesized from chemical precursors, natural dyes are mostly obtained from various plant parts. These dye-bearing materials contain only a small percentage of dye usually 0.5–5 %. These plant materials cannot be directly used for dyeing textiles. Also, many plant materials such as flowers and fruits are seasonal and contain a large amount of water and hence cannot be stored as such. Therefore, in order to make them suitable for textile dyeing purposes and to make them available throughout the year, these are subjected to some processing operations. Collected plant materials are first dried: either in shade or in a hot air drier at a low temperature of about 40–50 °C to reduce their water content to about 10–15 % or less. Many materials can also be sun dried. Dried material is then powdered in a pulverizer to reduce particle size and to facilitate better dye extraction. These powdered and dried materials in most cases can be stored in airtight bags and containers for at least a year and can be used for dyeing whenever required. Storage under nitrogen can further prolong their shelf-life. Many natural dye manufacturers sell such finely powdered materials and these are used by many cottage-level dyers practicing hand-dyeing as it works out cheaper. However, these powders are unsuitable for use in various dyeing machines such as a package dyeing machine as the textile material acts as a filter and the dye particles get trapped within it, resulting in patchy and uneven dyeing. Therefore purified dye powders are required for use in dyeing machines. For producing purified dye powders, dye has to be first extracted from dye-bearing materials and the extract thus obtained is then concentrated or dried to get liquid concentrates or purified ready-to-use powders. These purified forms are costly due to the involvement of various machines and increased consumption of energy in various processing operations. Also, the efficiency of dye extraction is less in comparison to the use of powdered crude dye-bearing material for dyeing as the dye extraction process also continues during the dyeing process. Various extraction and drying processes for production of purified natural dyes are described in the following text.

4.1 Extraction Methods

As natural dye-bearing materials contain only a small percentage of coloring matter or dye along with a number of other plant and animal constituents such as water-insoluble fibers, carbohydrates, protein, chlorophyll, and tannins, among others, extraction is an essential step not only for preparing purified natural dyes but is also required to be carried out by users of crude dye-bearing materials. As natural coloring materials are not a single chemical entity and the plant matrix also contains a variety of nondye plant constituents, extraction of natural dyes is a complex process. The nature and solubility characteristics of the coloring materials need to be ascertained before employing an extraction process. The different methods for extraction of coloring materials are:

- Aqueous extraction
- Alkali or acid extraction
- Microwave and ultrasonic assisted extraction
- Fermentation
- Enzymatic extraction
- Solvent extraction
- Super critical fluid extraction.

4.2 Aqueous Extraction

Aqueous extraction was traditionally used to extract dyes from plants and other materials. In this method, the dye-containing material is first broken into small pieces or powdered and sieved to improve extraction efficiency. It is then soaked with water in earthen, wooden, or metal vessels (preferably copper or stainless steel) for a long time usually overnight to loosen the cell structure and then boiled to get the dye solution which is filtered to remove nondye plant remnants. The process of boiling and filtering is repeated to remove as much dye as possible. When the extraction is to be carried out on a larger scale for preparation of purified dye powders, stainless steel vessels are used and the time of soaking the materials in water may be reduced by boiling the solution for an extended time period. Generally, centrifuges are used to separate residual matter. Use of trickling filters can ensure removal of fine plant material particles and ensure better solubility of the purified natural dye.

As most of the dyeing operations are carried out in aqueous media, the extract obtained by this method can be easily applied to the textile materials. Disadvantages of this extraction method are long extraction time, large water requirement, use of high temperature, and low dye yield as only water-soluble dye components get extracted whereas many dyes have low water solubility. Also, along with dye, other water-soluble substances such as sugars and the like get extracted that may have to be removed if the extract is to be concentrated and converted to a powder form. Yield of heat-sensitive dye substances gets reduced at boiling temperature, therefore a lower temperature should be used for extraction in such instances.

4.3 Acid and Alkali Extraction Process

As many dyes are in the form of glycosides, these can be extracted under dilute acidic or alkaline conditions. The addition of the acid or alkali facilitates the hydrolysis of glycosides resulting in better extraction and higher yield of coloring materials. An acid hydrolysis process is used for the extraction of dye from tesu (*Butea monosperma*) flowers. Acidified water is also used for extracting some flavone dyes to prevent oxidative degradation.

Alkaline extraction is suitable for dyes having phenolic groups as they are soluble in alkali, which improves the dye yield. Dyes can be later precipitated by the use of acids. Dye from annatto seeds can be extracted by this technique. This process is also used to extract lac dye from lac insect secretions and red dye from safflower petals [32]. The disadvantage of this process is that some coloring materials may be destroyed under alkaline conditions considering the fact that some of the natural dyes are pH sensitive.

Inasmuch as natural dyes are usually a mixture of different chemical constituents, changing the pH of the extraction medium by adding acid or alkali can lead to the extraction of different dye constituents which can lead to different hues upon subsequent dyeing and differences in colorfastness properties. Many researchers have studied the extraction of natural dyes under various pH conditions and compared the color and fastness properties of dyed fabric to find out the optimum dye extraction conditions and further additions to this information continue to be made every year in the scientific literature.

4.4 Ultrasonic and Microwave Extraction

These are actually microwave- and ultrasound-assisted extraction processes where extraction efficiency is increased by the use of ultrasound or microwaves thus reducing the quantity of required solvent, time, and temperature of extraction. When the natural dye containing plant materials is treated with water or any other solvent in the presence of ultrasound, very small bubbles or cavitations are formed in the liquid. These increase in size but upon reaching a certain size, they cannot retain their shape. When this happens, the cavity collapses or the bubbles burst creating high temperature and pressure. Millions of these bubbles form and collapse every second. The creation of very high temperature and pressure during extraction increases the extraction efficiency within a short time. Also the process can be performed at lower temperature and therefore extraction of heat-sensitive dye molecules is better. As exploration of new dye sources and attempts to optimize the dye extraction process is continuing, use of this extraction technique has been recently reported by many researchers [29, 31, 37, 38].

In microwave extraction, the natural sources are treated with a minimum amount of solvent in the presence of microwave energy sources. Microwave increases the rate of the processes so the extraction can be completed in a shorter time with better yield. Sinha et al. [53] have reported extraction of annatto colorant with microwave energy. Earlier their group had reported microwave-assisted extraction of blue pigment from the butterfly pea [52]. Microwave and ultrasound extractions can be considered as green processes due to reduction of extraction temperature, solvent usage, and time which results in lower consumption of energy.

4.5 Fermentation

This method of extraction uses the enzymes produced by the microorganisms present in the atmosphere or those present in the natural resources for assisting the extraction process. Indigo extraction is the most common example for this type of extraction. Freshly harvested indigo leaves and twigs are soaked in warm water (about 32 °C). Fermentation sets in and the colorless indigo containing glucoside indican present in the leaves is broken down into glucose and indoxyl by the indimulsin enzyme also present in the leaves. Fermentation is complete in about 10–15 h and the yellow liquor containing indoxyl is then taken to beating vats where indoxyl gets oxidized by air to the blue-colored insoluble indigotin which settles down at the bottom. It is collected, washed, and after removing excess water is pressed into cakes. Extraction of indigo from other indigo-containing plants such as woad is also carried out by fermentation. This process can also be used for extraction of certain other colorants such as annatto. The fermentation method is similar to aqueous extraction with the exception that this method does not require high temperatures. The microorganisms disintegrate the coloring matter binding substances in natural way. Long extraction time, need for immediate extraction of pigments after harvesting, foul smell due to microbial action, and so on, are some of the disadvantages of this method.

4.6 Enzymatic Extraction

As plant tissues contain cellulose, starches, and pectins as binding materials, commercially available enzymes including cellulase, amylase, and pectinase have been used by some researchers to loosen the surrounding material leading to the extraction of dye molecules under milder conditions. This process may be beneficial in the extraction of dye from hard plant materials such as bark, roots, and the like.

4.7 Solvent Extraction

Natural coloring matters depending upon their nature can also be extracted by using organic solvents such as acetone, petroleum ether, chloroform, ethanol, methanol, or a mixture of solvents such as mixture of ethanol and methanol, mixture of water with alcohol, and so on. The water/alcohol extraction method is able to extract both water-soluble and water-insoluble substances from the plant resources. The extraction yield is thus higher as compared to the aqueous method as a larger number of chemicals and coloring materials can be extracted. Acid or alkali can also be added to alcoholic solvents to facilitate hydrolysis of glycosides and release of coloring matter. Purification of extracted color is easier as solvents can be easily removed by distillation and reused. Extraction is performed at a lower temperature thus chances of degradation are fewer. The disadvantages of the method are the presence of toxic residual solvents and their greenhouse effect. Another disadvantage of this method is that the extracted material is not readily soluble in water and the subsequent dyeing process has to be carried out in an aqueous medium. Coextraction of substances such as chlorophylls and waxy materials also creates problem.

4.8 Supercritical Fluid Extraction

Supercritical fluid extraction is an emerging area in natural product extraction and purification. A gas functions as a supercritical fluid above its critical values of temperature and pressure. Such a fluid has physical properties somewhere between those of a liquid and a gas. They are able to spread out along a surface more easily than a true liquid because they have much lower surface tension than liquids. As their viscosity is also low, they have very good diffusivity and thus better interaction with the substrate. At the same time, a supercritical fluid is able to dissolve many substances like a liquid as solubility of a substance in any solvent is higher at higher pressure and temperature and such conditions are needed to maintain a gas in the supercritical state. Supercritical fluid extraction using carbon dioxide (CO_2) is a good alternative to solvent extraction as it is nontoxic, cheap, easily available, and does not leave residues. Critical temperature and pressure values for carbon dioxide are 31.4 °C and 1,070 pounds per square inch (psi) or 73.8 bars, respectively. Supercritical extractions using CO_2 typically operate at temperatures between 32 and 49 °C and pressures between 1,070 and 3,500 psi. As the CO_2 is a nonpolar molecule it behaves as does a nonpolar organic solvent. A cosolvent or a modifier may be added to improve the solubility of slightly polar solutes. The advantage of the process is that the extract is free from residual solvent traces and heavy metals and is light colored due to the absence of polar polymerizing substances hence the process has gained popularity in extraction of purified natural products for food and pharmaceutical applications. The disadvantage of the method is the high cost of the equipment and poor extraction of polar substances.

4.9 Drying Techniques

Coloring matter extract obtained from natural sources is mostly in aqueous media. If it is to be immediately used for dyeing as in many small-scale or cottage-dyeing establishments, it can be used as such after adjustment of concentration according to the shade requirements. However, if it is to be used at a later date for dyeing or in dye extract producing units, it has to be converted into either powder form or concentrated solid rich form for long-term storage and ease of transport. This also ensures uniformity of shade for the entire batch of dye powder or concentrate produced and natural dyes thus converted into powder form or liquid concentrates can be used like synthetic dyes by the industries. The following techniques are generally used for converting natural dye extracts into powder form or concentrates.

- Spray drying
- Drying under vacuum
- Freeze drying.

Spray drying is the most commonly used technique for converting natural dye extracts into powder form as it is simple and cost effective. The plant extract is sprayed into the spray chamber as fine droplets through an atomizer or spray nozzle. These droplets come into contact with hot air flowing into the chamber which removes the solvent; the resulting dry particles aggregate and fall to the bottom of the chamber where this powder can be collected. Natural dyes in ready-to-use dry powder form are mostly produced by this method. Dye molecules should be sufficiently stable to heat to follow this method of drying as dry powder is exposed to dry heat from the hot air. Also many fine dye particles that are too small to settle at the chamber bottom are carried away by the hot air and are lost resulting in lower recovery. Also higher dye content is needed to get larger size particles and lower losses that may be achieved by preconcentration of the extract or addition of inert compounds such as lactose and so on.

Extracts can also be concentrated under vacuum by use of a rotary evaporator or tray dryers and the concentrated dye can be purified further by the use of various solvents.

Another drying technique, lyophilization or freeze-drying can also be used for preparation of natural dye powders. In this process, the natural dye extract is subjected to freezing and water is removed from the frozen extract through sublimation by reducing the pressure. The equipment is costly and operating cost is also higher but heat-sensitive dyes can also be converted into dry powders as the process takes place at low freezing temperatures. Any one of the above techniques can be used for producing natural dye powder depending upon the dye extract properties and costs. Very pure dye extracts are now available for use in many countries especially the United States, but these are very costly and are mainly used by hobby groups for their uniqueness.

5 Application of Natural Dyes on Textiles

Natural dyes are mostly employed for dyeing of natural fiber textiles to enhance their eco-friendly characteristics. They are usually applied to textiles by dyeing. Apart from indigo, other natural dyes are usually not used for printing directly. For producing printed fabrics, the printing is usually done with mordant and the whole material is dyed whereby only the area printed with mordants picks up the color.

Natural dyes, like synthetic dyes, can also be used to dye textiles at all stages such as fiber, yarn, or fabric. Fiber dyeing has the advantage that any shade variation can be easily adjusted by blending and therefore has been practiced at industrial scale also but is costly due to problems in spinning and loss of dyed fibers. Wool is generally dyed in yarn form and traditional dyers prefer yarn dyeing for all materials as it offers versatility in designing during weaving. Dyeing in hank form is preferred by traditional dyers operating at the cottage level due to its simplicity and low investment and also its compatibility with their usage of crude dye-bearing natural resources for reasons of authenticity as well as cost effectiveness. Dyeing is normally carried out by these artisans by hand in large vessels. Iron, stainless steel, copper, and aluminum vessels are used. Dyeing in copper vessels is considered to produce bright shades. Aluminum vessels are normally stained with a particular dye hence should be used if only one type of dye is used. Stainless steel vessels are most preferred for the natural dyeing process. On a larger scale, hank-dyeing machines have been successfully used. Fine purified powders or concentrates are needed for package dyeing as otherwise dyeing is uneven. Fabric dyeing is also carried out in metal vessels at the cottage level. Machines such as the jigger and winch have been employed for dyeing larger lots.

Suitable dyes or dye-bearing resources are selected based on the color requirement. Information about some dye sources has been provided earlier. In general, tannin-containing barks are used to produce brown and grey colors. Flowers and leaves containing flavonoids are used to produce yellow color shades. Anthraquinone dyes from both animal and plant resources can be used for red color. Indigo is normally used to produce blue color shades. Secondary colors such as orange can be obtained by proper selection of dye and mordant or mixing two compatible dyes. However to get a green color or wherever blue color is needed to make a secondary color, material is first dyed with indigo and then overdyed with the other dye. If raw plant materials are used (which is usually the case at the cottage level), dye has to be extracted prior to dyeing. Details of various dye extraction methods have already been discussed. Aqueous-based extraction methods are employed. If purified natural dyes are used, these can be directly used for dyeing. The process for the dyeing of textiles with natural dyes differs from the synthetic dye application process because only some natural dyes can be applied directly to textiles. In most of the cases the dye is not substantive to the fiber on which it is being dyed therefore an additional step of mordanting is involved, making it a two-step process.

5.1 Mordanting

Textile fibers, especially cellulosics, do not have much affinity for the majority of the natural dyes; hence these are subjected to an additional step known as mordanting. Mordants are the substances that have affinity for both textile fibers and dyes, thus they act as a link between the fiber and dyestuff. Those dyes that do not have affinity for a fiber can be applied by using mordants. In the case of dyes having affinity for the fiber, the use of mordants increases the fastness properties by forming an insoluble complex of the dye and the mordant within the fibers, which also improves the color. Unlike animal fibers, vegetable fibers such as linen and cotton do not readily hold the mordants resulting in duller color compared to the bright colors obtained on wool and silk. Mordanting is very important for cotton as it is more difficult to dye than wool or silk due to the absence of amino and carboxyl groups that provide attachment sites to dye molecules. There are three types of mordants, namely metal salts or metallic mordants, oil mordants, and tannins which are discussed below.

5.2 Metallic Mordants

Metal mordants are often used for the dyeing of textiles with natural dyes. Metal salts of aluminum, chromium, tin, copper, and iron were being used as mordants by traditional dyers. Now chromium has been red-listed under eco-regulations and therefore should not be used to maintain the eco-friendly nature of dyed textile material as well as the discharged effluent. Copper is also in the restricted category but its permissible levels are higher and can therefore be used in small amounts so as not to cross the permissible limit on dyed textile. Tin is not restricted by many eco-labels but its presence in effluent is not desirable from an environmental viewpoint. Alum and iron can be considered ecologically safe mordants as they are naturally present in the environment in large amounts.

Different colors from the same dyestuff can be obtained by use of different metallic mordants because color obtained with many natural dyes is due to the formation of colored insoluble dye complexes with metal salts or mordants. Dye complexes with different metals have different colors and may also differ in fastness properties. For example, alizarin forms a red lake or complex with aluminum and a violet lake with iron. Similarly, onion natural dye which is yellow in color will change to orange color with stannous chloride mordant and grey color with ferrous sulphate. Information about some metallic mordants is provided below.

5.3 Aluminum

Potash alum, which is the double sulphate of potassium and aluminum, is the most widely used aluminum mordant for natural dyeing. It can be used alone or with cream of tartar or as basic alum for mordanting. When used alone, the material before dyeing is merely boiled in a solution of alum. The amount of mordant required depends on the shade to be dyed. If deeper shades are being dyed, more mordant is needed. Generally 10–20 % of alum can be used on the weight of the material (owm). If used along with cream of tartar, alum powder (20 % owm) is mixed with cream of tartar (40 % owm) in a little warm water and diluted to the required volume.

Alum in the form of basic aluminum sulphate (neutral alum) is used as a mordant for cotton. It is prepared by adding sodium hydroxide or carbonate solution to the aqueous solution of alum till the precipitate formed redissolves upon stirring. The material to be treated is dipped in the alum solution and the latter is then fixed by other chemicals or ageing. It is preferable to fix the alumina on the fiber by precipitating it with salts such as sodium carbonate or sodium phosphate to obtain good dyeing results. Neutral soap solution can also be used.

In another method the material is dipped in vegetable tannins/tannic acid or oil mordant such as Turkey Red Oil (TRO) before treatment with basic alum which results in good fixation of aluminum. Other aluminum salts such as aluminum sulphate or acetate can also be used for mordanting.

5.4 Iron

Iron salts in the form of ferrous sulphate (also known as green vitriol or copperas) are extensively used in dyeing and printing. Application of iron salts imparts a black or grey color to the fabric and dulls the shade. Ferrous sulphate if applied alone leaves only a very small quantity of iron on the fabric. Tannin-pretreated cotton picks up a good amount of iron. Cream of tartar can be used along with iron to fix it on the animal fibers. Traditional dyers use a fermented iron solution for iron mordanting where iron is present as acetate.

5.5 Copper

Copper sulphate or blue vitriol is generally used for copper mordanting. It is known to improve the lightfastness of various natural dyed materials and is necessary to obtain brown color from catechu and black color from logwood according to traditional recipes. As eco-standards limit the content of extractable copper in textile materials to 3–100 ppm depending upon the standard and clothing type, it should be used judiciously in small amounts.

5.6 Tin

Tin mordant brightens the color. Stannous and stannic chloride are used as mordants. Stannic chloride is preferred for cotton. It is generally used on tannin-pretreated cotton. For wool, cream of tartar may also be added to the bath. Although not restricted by many eco-standards, its use is not recommended from an environmental pollution viewpoint. It is not permitted to be used under the recent Global Organic Textiles Standard (GOTS) where its amount has been restricted to below 0.2 ppm.

5.7 Chromium

Earlier used by many dyers in the form of potassium dichromate and referred to as Chrome, its presence on textiles is now restricted by most of the standards to a level of >0.2 ppm, therefore it is better to avoid this mordant.

5.8 Oil Mordants

These mainly find application for dyeing madder to obtain Turkey red color. Alum is the main mordant used here. It gets fixed onto the cotton material by forming a complex with the oil mordant and then combines with madder to produce the Turkey red color. In the past, castor and til (sesame) oils were used as mordants but they were later replaced by Turkey Red Oil (TRO) which is sulphonated castor oil.

5.9 Tannins and Tannic Acid

Tannic acid or tannins are used as a primary mordant for cotton and cellulosic fibers as they do not have much affinity for metallic mordants. A cotton fabric treated with tannic acid can absorb all types of metallic mordants. Tannins may be in the form of tannic acid or vegetabl-tannin–containing substances such as myrobolan (Harda, *Terminalia chebula*), oak galls, sumac, or pomegranate rind may be used for mordanting. Vegetable tannins are cheaper and occur as excretions in the bark and other parts such as leaves, fruits, and galls. The tannin in myrobolan is of the ellagitannin type and occurs mainly in the peel of the fruit. It also contains a yellowish-brown coloring matter that imparts a yellowish coloration to textile material. It is widely used as a mordant in the dyeing of cotton and for producing black shades. Leaves and twigs from various species of *Rhus* or sumac contain 15 to 20 % tannin which is of the gallotannin type. It has an olive-green color. The presence of some reddish coloring matter in sumac prohibits it from being employed for light and brilliant shades.

5.10 Mordanting Methods

There are three types of methods for application of mordants based on the time of their usage. They are:

1. Premordanting
2. Postmordanting
3. Metamordanting or simultaneous mordanting.

As suggested by the name, in premordanting, the mordants are applied to the fabric prior to dyeing. It is most common for cotton and cellulosics as in the unmordanted state they do not have affinity for many natural dyes. Even for animal fibers, some natural dyes such as cochineal require this type of mordanting process for producing good shades. Various famous traditional printing styles with natural dyes from India such as “Kalamkari” in Andhra Pradesh and “Sanganeri” in Rajasthan use this mordanting method. The advantage of this method is that standing baths can be used for mordanting; that is, the bath can be reused many times after replenishing with the mordants. This makes the process economical as well as reduces the pollution load hence is useful for large-scale applications.

In the postmordanting method, the fabric after dyeing is treated with mordant in a separate bath. The final color is developed during the last phase. Iron salts are very often applied in this manner for producing grey and black colors.

In the metamordanting or simultaneous mordanting method, both dyeing and mordanting processes are carried out in the same bath itself. Usually for cotton and cellulosics, mordant is also added to the dye bath at the start of dyeing so that both dyeing and mordanting processes take place simultaneously in the same bath. For animal fibers such as wool, mordant may sometimes be introduced into the dye bath towards the end of the dyeing process when much dye has already been exhausted onto the textile. The dyeing duration is reduced in this method due to a reduction in the number of steps. This method produces darker shades for some dyes whereas for others, color yield may reduce due to the loss of some dye and mordant to dye–mordant complex formation in the dye bath which may also cause uneven dyeing. As the mordant cannot be reused, this process is more useful for small lots.

5.11 Dyeing

As for synthetic dyes, the amount of dye to be taken is normally given as % shade. It denotes the amount of dye (in grams) to be taken for dyeing 100 g of textile material. The terminology remains the same for both crude dye material and purified extracts. As the dye content of raw materials is low, it is common to use 10–30 % shade whereas the amount can be reduced to 2–5 % for the purified dye extracts. The amount of mordants is also selected in relation to the shade dyed. A larger quantity of mordants is needed for higher shades.

As is the case with synthetic dyes, the amount of water to be taken in the dye bath is an important parameter. In technical terms, it is given in the recipe as the material-to-liquor ratio (MLR). The MLR denotes the amount of water in ml required per gram of the fabric to be dyed.

As natural dyes differ in their chemical constituents, their dyeing procedures also differ but their basic dyeing process is similar. There may be different optimum temperature, time, and pH of dyeing but the basic steps remain the same. Many natural dyes are dyed at near boiling temperature on cotton. Wool and silk are dyed at a lower temperature although some dyes may dye cotton also at lower temperature. Most dyes require neutral pH but some dyes require acidic pH and some may need alkaline pH. For dyeing animal fibers wool, pashmina, and silk, generally 1–2 % of acetic acid is added during dyeing. The material to be dyed premordanted or otherwise is introduced into the dyeing bath at room temperature and the temperature is then increased slowly to ensure uniformity of dyeing. The material is usually dyed for at least an hour to allow the dye to penetrate well inside the textile material. The movement of textile material in the dye bath is very essential. If the dyeing is carried out in dyeing machines, movement of the material is taken care of but in hand dyeing, the fabric needs to be continuously stirred in the dye bath, otherwise uneven dyeing may result. If delicate fabrics such as pashmina are to be dyed, the dye bath should not be stirred continuously as that will damage the fabric structure. In such cases, it is advisable to have a material-to-liquor ratio of at least 1:100 so that the fabric is completely immersed in the dye liquor during dyeing and dyeing is uniform. If simultaneous mordanting is to be carried out, the required quantity of mordant is also added to the dye bath. After the dyeing is over, the dyed materials are removed and allowed to cool down a little and then washed with water. Some traditional dyers leave the material in the dye bath itself to cool and then remove the material for washing. The washed dyed material is then soaped with a hot soap or nonionic detergent solution to remove loosely held dye and is again rinsed with water and air dried in shade. At industrial scale, hydroextractors are used to remove excess water during washing. If post-mordanting is to be carried out, the washed material is taken up for postmordanting without soaping and soaping is carried out on the postmordanted material after washing. When cotton materials are dyed with dyes such as madder which do not have affinity to it without mordants, the premordanted dyed material may be further postmordanted to get different shades and improvements in fastness properties. Treatment with small amounts of copper mordant improves the fastness to light for many dyes although it also results in slight hue changes. Such treatment with copper to improve lightfastness was also practiced earlier for certain synthetic dyes. A postdyeing treatment with tannins and alum can help in improving the fastness to washing.

5.12 Indigo Dyeing Process

The indigo dyeing process is different from the general natural dyeing process using mordants or direct dyeing as it is a vat dye. That is the reason why indigo dyeing cannot be combined with any other natural dyeing process. The process for indigo dyeing consists of reduction of indigo to its leuco form which is soluble in alkali. In olden days, a fermentation process was used to reduce the indigo and seashells, limestone, plant ashes, or alkaline earth provided the alkali for its dissolution. Continuous vats were maintained continuously for a number of years in which indigo-reducing microorganisms thrived. Indigo and other materials were added to these vats before dyeing as per the requirement. Nowadays, only some dyers maintain the traditional fermentation vats for small-scale applications. Mostly, reducing agents used for reducing synthetic indigo including hydrosulphite, thiourea, and the like are also being used for natural indigo and caustic soda is used as alkali. After reduction, the materials to be dyed are immersed in the bath and dyeing is continued for the stipulated time, which is usually a few minutes. Finally, the materials are removed from the bath and exposed to air to oxidize the leuco form of indigo to its original insoluble blue form. These are then soaped to remove unfixed dye thereby improving the rubbing fastness, rinsed with water, and air dried in shade.

6 Advantages of Natural Dyes

Natural dyes are considered to be eco-friendly as these are obtained from renewable resources as compared to synthetic dyes which are derived from non-renewable petroleum resources. These are biodegradable and the residual vegetal matter left after extraction of dyes can be easily composted and used as fertilizer. They produce soft colors soothing to the eye which are in harmony with nature.

In addition to these environmental benefits, natural dyes also offer functional benefits to the wearer and users of such textiles. Many of the natural dyes absorb in the ultraviolet region and therefore fabrics dyed with such dyes should offer good protection from ultraviolet light. Improvement in UV protection characteristics of natural cellulosic fibers after treatment with natural dyes has been reported by various researchers [11, 28, 47]. Griffony et al. [16] observed that treatment with tannins during mordanting itself improved the UV protection of fabrics. Saxena et al. [50] also observed that extracts of tannin-rich pomegranate rind showed strong absorption in UV region and cotton fabrics treated with these extracts showed excellent UV protection which was durable to washing. As cotton and other cellulosics are frequently treated with tannins in the mordanting step during dyeing with natural dyes, it is likely that such dyed fabrics would also show good UV protection. Many of the natural dye materials possess antimicrobial properties. Therefore, textiles dyed with such materials are also likely to show antimicrobial properties and the same has been reported by many researchers [12, 18, 36]. Ibrahim et al. [25] have reported improvements in both UV protection and antibacterial activity for polyamide 6 fabrics after treatment with natural dyes. Fabrics dyed with some natural dyes have been reported by the wearers to be free of odor perhaps due to the antibacterial or bacteriostatic properties of natural dye materials. Users of natural dyed fabrics have also found such fabrics to be mosquito repellent and/or moth repellent as perhaps the plant material from which these dyes were derived might also have contained natural repellent substances. In addition, recently, cellulosic textiles treated with natural plant extract have been found to exhibit flame-retardant properties [4].

Many natural dyes such as myrobolon fruits, turmeric, manjishth root, Arjuna (*Terminalia arjuna*) bark, and safflower florets, among others possess curative properties and have been used in various traditional medicinal systems. Textiles dyed with these materials may also possess healing properties by absorption of medicinal compounds through the skin. Textiles produced in Kerala, India by dyeing with herbs as per the traditional Ayurvedic system of medicine and known as “Ayurvastra” have become very popular as health and well-being textiles and also as medicinal or curative textiles and are being exported to various countries. Various companies are now marketing naturally dyed textiles as health and well-being textiles.

7 Drawbacks of Natural Dyes

Natural dyes are considered to be an eco-friendly alternative for dyeing of textile materials, especially natural fiber textiles. However, there are many limitations in the usage of natural dyes some of which are listed below.

7.1 Tedious Application Process

Natural dyes require a longer dyeing time in comparison with synthetic dyes as very often an additional mordanting step is required. Use of raw dye-bearing materials ensures authenticity but at the same time involves additional dye extraction steps that require time and separate set-up. Natural dyes in this form are also not suitable for use in many commercial textile dyeing machines which makes the process labor intensive. Also in an industrial set-up, disposal of solid residual biomass is problematic. Purified extracts, although suitable for machine application, are costly and not economical. Logistics for making agricultural by-products such as pomegranate rind, onion skins, or fruits and leaves of trees from the forests available for dyeing purposes are not in place which would have helped in reducing the costs. Exhaustion of most of the natural dyes on textile materials is poor in spite of using the mordants which leaves a large quantity in the dye bath after dyeing. That increases the cost of dyeing although it may not have other environmental implications as seen for synthetic dyes due to the biodegradable nature of these dyes. Traditional dyers reused the dye bath but the color obtained is different from the earlier lot which may not be acceptable by today’s standards. All these increase the cost of naturally dyed textiles.

7.2 Limited Shade Range

Shade range of natural dyes is limited. Out of the three primary colors—red, yellow and blue—although there are several sources for red and yellow dyes, there is only one major source of the blue dye: indigo. As natural dyes differ in their application process, only few dyes can be applied in mixtures and differences in fastness properties further limit the choice. Even a common secondary color such as green needs to be produced by overdyeing as blue dye indigo being a vat dye has an entirely different application process that increases the dyeing time and cost.

7.3 Nonreproducible Shades

Difficulty in reproducing the shades is another major drawback of natural dyes which is caused by the inherent variations in the proportion of chemical constituents in the natural material and thus in its crude extract depending upon the maturity, variety, and agroclimatic variations such as soil type, region, and so on. Therefore it is not possible to produce the same shade with a particular natural dye in every dyeing operation [51]. Production of standardized dye powders is an expensive and complicated exercise as most of the natural dyes contain various chemical constituents. Some of the natural dyes are pH sensitive and tend to change color due to change in pH. As natural dyes tend to form colored complexes with metal ions, the mineral composition of water may also cause shade variations. Hence even the same standardized powder may give different shades at two different places due to the differences in mineral content and pH of the water which makes it very difficult to reproduce the shades.

7.4 Fastness Properties

Colorfastness to light and washing are most important parameters to evaluate the performance of a textile and deciding about its end use although colorfastness to rubbing and perspiration are also important especially if it is to be used as apparel. A material should have good fastness to light if it is to be used for making curtains although a little lower fastness to washing may be satisfactory for this application. Colorfastness properties of natural dyes are a cause of concern. Only a few natural dyes possess fastness properties conforming to modern textile requirements. Restrictions on the use of certain metal salts for mordanting such as chromium, copper, tin, and so on by eco standards has not only reduced the color gamut of natural dyes but has also made the task of producing shades with good fastness properties difficult. Improper application procedures used by certain practitioners of natural dyes are also sometimes responsible for poor fastness properties. Improvements and optimization of mordanting and dyeing procedures can help in solving this issue. Exploring the new sources for dyes can increase the number of dyes with better colorfastness properties.

7.5 Safety Issues

Exploration of new sources for dyes can certainly help in increasing the shade range of natural dyes with good fastness properties. However, extensive research on the safety of these materials to humans and the environment would be needed before propagating their usage as everything of natural origin may not be safe.

Nature is known to produce poisonous substances also; therefore thorough toxicological evaluations for the new sources are necessary. Use of metallic mordants also requires caution so as not to cause adverse health effects during handling. Precautions should also be taken to prevent pollution problems in the usage of these mordants and it should be ensured that the amount of restricted mordants in the dyed textile is within the limits set by eco regulations.

7.6 Characterization and Certification Issues

Although dyeing of textile fabrics with dyes obtained from various natural resources has been extensively investigated, little information is available on the identification and characterization of the natural dyes. Natural dyes, being plant metabolites, are present only in small amounts in dye-bearing materials along with large quantities of other nondye materials. The dye content may vary according to the age, part of the plant, and agroclimatic conditions, and it is important to know the dye content in order to get reproducible shades. While procuring the dye materials, pricing should match the dye content and when powdered dye materials or extracts are used, these should be authentic. Thus determination of dye content as well as characterization of dye material is important in the case of natural dyes. Absorption spectroscopy is very successfully used for measuring the dye content of synthetic dyes but has limited applicability for natural dyes as these dyes are usually not a single chemical entity but a mixture of closely related compounds and in many cases there are no clearly defined absorption maxima. A literature survey shows that the earliest attempts to characterize the natural dyes were made in the context of identifying the dyes present on historical textiles kept in museums or those found in archaeological excavations. Different techniques including high-performance liquid chromatography (HPLC), thin-layer chromatography (TLC), high-performance thin-layer chromatography (HPTLC), UV visible, and mass spectroscopy have been employed for this purpose [13, 46]. However, there are no certification bodies or any testing agencies that can certify or characterize and identify the commercial natural dyes or the fabrics dyed with natural dyes although such fabrics fetch higher prices. As a result, some unscrupulous elements in the trade tend to mix natural dyes with cheap synthetic dyes or try to pass off the fabrics dyed with synthetic dyes as those dyed with natural dyes. It is quite common to find people trying to market fabrics dyed with synthetic alizarin or indigo as dyed with natural dyes. Therefore development of process protocols for quick identification and characterization of natural dyes is very important for the sustainability of true natural dyed textiles. TLC and HPTLC techniques can be easily employed for quick identification of natural dyes by comparing with chromatographic fingerprints of authentic natural dye samples. Many organizations have worked in this direction and in authors' lab HPTLC fingerprints of root and stem samples of *Rubia cordifolia* and *Rubia sikkimensis* were also developed which are presented in Fig. 8.

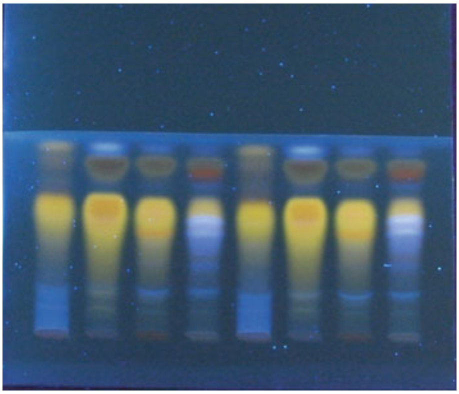

Fig. 8 HPTLC fingerprints of *Rubia* spp. root and stem

Establishment of some certification system such as those followed for organic crop products would be very helpful in this regard as that can ensure both authenticity and quality because often the fastness properties of natural dyed materials are not satisfactory due to improper dye application procedures. Such a certification system has been established in Turkey under the DOBAG project where the University of Marmara is ensuring the quality of each natural dyed carpet having the DOBAG tag.

8 Present Scenario and Sustainability Issues in Usage of Natural Dyes

Presently natural dyes are not in use for mainstream textile processing. Only about 1 % of the total textiles produced are dyed by using natural dyes [20]. Traditional dyers, enthusiasts, and hobby groups are the main users of natural dyes who work at the cottage level. Some small industries are also using natural dyes and there are a number of companies who are manufacturing and selling natural dyes both as finely ground plant material as well as purified extracts. Sustainability is a complex multidimensional concept concerning the environment, economy, human health, and social impact. It aims to meet the needs of the present generation without compromising the ability of future generations to meet their needs. According to Hill [23] greater emphasis on using natural dyes in the textile industry can make a valuable contribution to the environmental sustainability in the twenty-first century. Various sustainability issues involved in the present status of usage of natural dyes and in its further promotion are discussed in this section.

8.1 Renewable and Biodegradable

Natural dyes are obtained from natural resources, mainly different parts of the plants which unlike petroleum resources are renewable. Some of the dyes including turmeric, safflower, marigold, and indigo are obtained from annual plants and thus are renewed annually. Many dyes derived from flowers and fruits and seeds of trees such as myrobolon, tesu or flame of the forest, annatto, and the like, also are renewed annually. Tree leaves are also a sustainable and renewable source, provided these are harvested in a scientific manner and quantity and frequency of leaves removed from each tree does not exceed its renewal potential. The removal of leaves is not as harmful to the plant as the stripping of bark [39]. Deciduous tree leaves are again annually renewable. Bark and wood are not sustainable sources in the sense that removing these without harming the tree is difficult. However, these can be obtained as by-products from the timber industry and new plantings of such plant materials need to be made to ensure sustainability. Some dyes such as safflower florets, onion skin, and pomegranate rind, among others are an agricultural by-product and other than the collection and transportation costs, no other investment is needed in their use as natural dyes. Pomegranate rinds are an agroprocessing by-product. Temple waste flowers also offer an inexpensive source of natural dyes [58]. Lac is an industrial by-product as it is recovered from the washwaters of the shellac-processing industries. Exploration of ways and means to utilize these resources for enhancing the availability of natural dyes is much required as that would also provide additional income and empower the farmers and small scale entrepreneurs.

Natural dyes are biodegradable as they are derived from natural materials and can be easily degraded by microbial action. The dye molecule on its own is weakly colored and is susceptible to the action of light and water. It is due to the complex formation with the mordant that deep coloration is obtained and good resistance to the action of light and water in terms of improved fastness to light and washing is achieved. However, in the case of synthetic dyes, the dye molecule in itself is designed to have brilliant color and good resistance to the action of light and water. It is the good performance of these synthetic molecules as a dye on textiles that makes them difficult to degrade thus making the treatment of the effluent containing their residual amounts extremely difficult.

8.2 Easy-to-Treat Effluent

As natural dyes are biodegradable, and complex chemical auxiliaries and extreme pH conditions are not used in the dyeing process, effluent produced during their usage is considered to be easily treatable and expensive elaborate effluent treatment plants needed for synthetic dyes are not required. Data presented by Henriques and Shankar [22] confirmed it. The effluent produced by using different natural dyes was found to have a BOD value of 40–85 mg/L only which was less than the limit of 100 mg/L prescribed by the Central Pollution Control Board (CPCB), Government of India. It also had no color and its TSS and TDS levels were much below the levels reported for various classes of synthetic dyes. Most parts of the TDS also consisted of various plant nutrients such as potassium, calcium, sulphate, and the like and hence were successfully used for irrigation of plants. Earlier, it was reported in a pilot-level study conducted on the dyeing of cotton with dye extracted from dried chrysanthemum flowers, that COD of the dye effluent was reduced by almost 75 % within a day upon simple storage and by next day its level came down to below 20 mg/L which was the limit prescribed by the CPCB, India in respect of BOD for discharge into inland water bodies 49]. A reduction in pollution load with plant-based dyes in comparison to the application of synthetic dyes even with latest dyeing techniques has been reported by Bechtold et al. [5]. Thus these dyes are advantageous to the rural artisans practicing traditional craft forms in remote areas as they can use locally available resources for coloration of textile materials. As they do not have access to complex effluent treatment solutions, easy biodegradability of these dyes reduces the risk of polluting the local water resources and offers a clean production model.

8.3 Promote Vegetation and Carbon Fixation

As natural dyes are mostly derived from plant parts, higher usage of natural dyes would lead to the planting of more dye-bearing plant materials which would lead to higher carbon fixation in the form of biomass synthesized by these plants. Generally only a part of the plant is used for dyeing purposes and that too contains at most 5 % of dye. Therefore for every kilogram of natural dye produced, some other useful products can also be obtained if purified dyes containing only the specific dye components are isolated. Also, if the enormous quantity of biomass produced is composted, it would help in improving soil fertility and agricultural production and thus further increase the carbon fixation. The UNDP-sponsored project implemented in India during 1998–2001 listed more than 100 promising natural dye materials, many of which were suitable for revegetation of wastelands [3]. Thus cultivation of dye-yielding plants may be practiced for the greening of the wastelands and thereby enhancing the carbon fixation. The SPINDIGO (sustainable production of plant derived indigo) project implemented in Europe in the beginning of this century involving 10 institutions from five countries found that production of plant- (woad-) derived high-purity indigo is a viable alternative and such indigo can meet about 5 % of total indigo consumption in Europe. Farmers can be given seeds and agronomic packages for improved indigo content of the produce and cultivation of indigo can provide a good source of income to the farmers. Similarly, farmers in the other parts of the world can grow dye-yielding crops and trees that would enhance their income and also help in promoting vegetation and hence carbon fixation. Similar observations were made in respect to other dye-yielding plants such as weld and madder also in other projects implemented in the European Union during the first decade of this century. However, due to problems with the consistency of raw plant products, actual commercial production of such crops for industrial-level application could not pick up.

8.4 Status in GOTS

All natural dyes except those derived from a threatened species are recommended for coloration of organic textiles according to the latest (3.0) version of Global Organic Textile Standards (GOTS). However, it is also specified that all dyed textiles should fulfill the norms with respect to restricted heavy metal content and colorfastness requirements and their production should not lead to environmental contamination. Therefore, not all natural dyes would be able to fulfill these criteria. Natural-dyed textiles where chrome or tin is used as mordant would not be able to pass the test for restricted heavy metal content and those with copper mordant would need careful monitoring to ensure compliance. Also natural-dyed fabrics not matching up to required levels of fastness to rubbing, perspiration, washing, or light are also not eligible for this certification. At the same time, all safe synthetic dyes that do not contain the banned aromatic amines or prohibited heavy metals are also allowed provided the effluent meets the criteria prescribed by the local regulatory bodies. This does not confer any special status to natural-dyed textiles. A separate sublabel for natural-dyed textiles in this standard would have been of much help in promoting the cause of natural dyes as it would have provided incentives to those practitioners of natural dyes who would have been able to meet the technical performance specifications and environmental requirements.

8.5 Availability and Supply Issues

Availability and supply of natural dyes is of major concern from the sustainability angle. At the present level of world textile production, natural dyes can only replace a fraction of total textile dye consumption. The tedious process of color extraction and seasonal availability of natural dye sources are the reasons hindering their use in textile coloration. In order to reduce the problem and to ensure ready availability of natural dyes, they have to be converted into ready-to-use soluble powders or liquid concentrates just like synthetic dyes. By converting into powder form, the shelf-life of natural dyes can also be increased. Many companies in the United States, India, and China are presently selling natural dyes as both raw material powders and ready-to-use extracts and these can be ordered on the Internet. Ready-to-use dyes are, however, very costly. It is possible to exploit the by-products and waste material from the food processing industry such as pomegranate rinds, onion skins, grape skins, and the like for extracting natural dyes as the problem of ready availability at a place gets solved and the costs can be reduced. A collection and supply mechanism for some agro by-products such as safflower florets as also for forest products such as myrobolon fruits, tree leaves, and so on needs to be established to increase their availability. Some important dye plants including madder and indigo can be cultivated on marginal and wastelands to enhance their availability and good income for cultivators. Better agronomic practices and high color-yielding varieties with respect to such plants need to be developed to make the production economical. Some initiatives in this direction were undertaken in Europe some years back whereby it was observed that cultivation of plants such as woad, weld, madder, and so on for producing dyes is economically feasible but guidance for growers and establishment of forward linkages in the form of processing units is needed. Land availability for growing natural dyes is, however, limited in view of the first preference to food and fodder crops and therefore microbes offer tremendous potential for the supply of natural colorants. Biotechnological tools can be of great help in this regard by identifying and transferring the dye-producing genes into fast-growing harmless microbes. Due caution about the safety and toxicological aspects, however, is needed.

8.6 Danger of Deforestation Due to Indiscriminate Exploitation

Promotion of natural dyes without ensuring the increased availability of dye-bearing resources carries the danger of overexploitation. It is in this context that GOTS prohibits the use of dyes and auxiliaries from the bioresources on the endangered list. Many dyes are obtained from tree bark, wood, and roots and it is difficult to obtain them without damaging the plant. Harvesting only a small portion or obtaining these materials as a by-product from the timber industry may be sustainable but indiscriminate harvesting and tree cutting to get these materials for dyeing purposes is sure to damage trees and lead to deforestation. It takes a number of years for a tree to grow, therefore unless these trees are planted in greater numbers before harvesting the existing ones biodiversity would be greatly endangered. Although leaves are a more sustainable resource than bark or roots, frequent indiscriminate harvesting of leaves may also cause damage to the trees. Use of flowers has the danger of disturbing the natural pollination and reproduction cycle of plant species. Harvesting of fruits and seeds does not affect the plants but care should be taken to use only such fruits and seeds that are not eaten by animals and birds otherwise their natural food sources would be lost. It is observed that many tribal people who live on the edges of the forest area have learned to live in harmony with nature. They fulfill their needs by obtaining forest produce only to the extent required for their needs and leave the rest undisturbed. This balance may be disturbed by the lure of money from the sale of dye resources which may lead to deforestation unless the people are trained in sustainable harvesting of dye plants and such harvesting is closely monitored to prevent overexploitation at the instance of dye manufacturers. Such efforts were made in an ICEF-funded project in India [22] where tribal people were trained in sustainable harvesting of dye-bearing tree leaves. They were further trained in the drying of these leaves and these dry leaves were then supplied to a natural dye manufacturing unit that in return provided them with cooking gas cylinders which eliminated the cutting of forest trees for firewood by these people leading to improved forest cover rather than deforestation.

8.7 Use of Non-Eco-Friendly Metallic Mordants

The use of metallic mordants during natural dyeing often puts a question mark on the eco-friendliness of natural dyes. Only a small amount of these metal salts gets fixed onto the textiles and the rest is discharged as effluent which leads to the contamination of land and water resources. However, it has been observed that out of the five metallic mordants traditionally being used for natural dyes, alum and iron are environmentally safe and these have not been restricted by any eco-regulations. In fact they are used for effluent treatment of synthetic dyes. Out of the remaining three mordants, chromium as Cr VI is very toxic, hence should not be used. Tin should also be avoided; copper may, however, be used judiciously as it has a higher tolerance limit in various eco-regulations. Of course the effluent should contain as low an amount of the mordant as possible to avoid pollution problems. Creation of awareness about this aspect among traditional dyers using natural dyes is important to make the naturally dyed textiles eco-friendly. Use of standing baths for these mordants can minimize the pollution problems but it would require working out the exact amount exhausted onto the fibers so as to facilitate replenishment. Traditional recipes need to be reworked for maximizing the mordanting bath exhaustion so that lower quantities can be used and there is less mordant to be discharged as effluent. Use of some auxiliaries such as formic acid or cream of tartar can improve the uptake of metal ions by the animal fibers and a pretreatment with tannin substances can improve the metal ions pick-up by cellulosic materials. At the same time, it should also be ensured that the amount of restricted metals on the fabric is within the prescribed eco limit. Extensive reworking of mordanting and dyeing recipes is also needed so that the required level of fastness properties could be achieved while maintaining heavy metal mordant content within the limits suggested by eco-regulations. In order to make natural dye sustainable, it would be very important if metallic-salt–based mordants can be replaced with natural mordants. Several research studies have attempted to use tannin-based natural substances such as myrobolan, tannic acid, and pomegranate rind as natural mordants in place of metallic mordants and these were found to be effective in improving the fastness properties. Thorough research and transfer of research results to actual users is necessary to stop the usage of non eco-friendly mordants.

8.8 Unsuitable for Industrial Set-Up

Natural dyes presently are not suitable for industrial set-up due to the tedious application process of raw natural resources. These materials are not compatible with many industrial dyeing machines hence the dyeing process becomes labor intensive. Also the availability of many natural dyes is also not sufficient as in many cases a proper supply chain is not in place. A range of shades with good fastness properties is limited. They are not suitable for working in mixtures and not amenable to shade matching and prediction with the help of computerized color-matching systems. Therefore these are mostly being used by practitioners of craft forms, hobby groups, and NGOs only on the cottage level. Today's high cost of purified natural dyes makes their industrial use an impractical proposition.

8.9 Cost Considerations

Presently the cost of dyeing textiles with natural dyes is much higher in comparison to the cost of dyeing with synthetic dyes due to several reasons. First the application procedure is lengthy and complicated. Most of the dyeing is done by hand hence it is labor intensive. The dye yield of colorants is not good and a much larger amount is needed to get good shades, whereas synthetic dyes are intensely colored and a much smaller amount is sufficient to produce good coloration. The cost of the dye material itself may be more as sometimes it is already in use for other purposes such as traditional medicine, food ingredients, and the like. Only few dyes have a similar application technique so that if two dyes are needed to produce a shade, dyeing has to be carried out twice which increases the cost. Also due to the small level of operations, economy of scale is not achieved. However, if the hidden cost of the use of synthetic dyes in terms of pollution caused and its detrimental effects on the environment or the investments made and expenditure incurred on effluent treatment is also considered, the gap substantially narrows down. According to the study conducted by Nayak [34] under the ICEF-funded project executed in India, the hidden environmental cost for synthetic dyes works out to be Rs. 410/kg of dye and if this cost is to be incurred by synthetic dye manufacturers, production of these dyes would become unsustainable. According to the same study, the cost of dyeing textiles in blue, black, and yellow shades with natural and synthetic dyes is almost comparable and only the cost of dyeing red is slightly higher for natural dyes when environmental cost is also taken into account. Natural dyed textiles presently sell at a premium, but this is only a partial compensation towards the environmental health and social benefits associated with the use of natural dyes.

8.10 Human Health and Safety Aspects

As textiles are worn next to the skin, the substances present on these can get absorbed by the skin and affect the health of the wearer. Skin irritation and contact dermatitis have been reported for some synthetic dyes and the use of azo dyes made from carcinogenic amines has been banned by legislation in many countries. Production of synthetic dyes involves the use of many toxic and hazardous chemicals and harsh conditions, and adequate protection measures for the workers and proper effluent treatment and disposal systems are needed. Many natural dyes, on the other hand, have been used as medicines in traditional medicine systems; it is therefore likely that textiles dyed with these dyes may have a beneficial effect on health. People using naturally dyed textiles have reported their positive effects on health although detailed systematic studies on this aspect have not been conducted. Care, however, is required when new dye sources are introduced and detailed toxicological studies have to be undertaken to establish their safety to humans and environment. Also, the production process of these dyes does not use harsh chemicals and uses mild conditions, therefore there is no adverse effect on the health of the workers. On the contrary, it may have a positive effect on health in view of the therapeutic and medicinal value of dye-bearing plant materials. The presence of pesticide residues in natural dyes from the usage of pesticides to control insects and pests and content of restricted heavy metals in dyed material from the soil or from the mordanting process during dyeing are aspects that need monitoring from the human health viewpoint.

8.11 Social Issues

Synthetic dyes seem to be cheaper today but according to the study by Nayak [34] if their impact on the environment and health of people is considered, their cost increases by almost INR 410 per kg of dye. It is common knowledge that dyeing operations in developing countries are mostly carried out in small-scale industries that discharge highly polluted effluent in nearby water bodies or land with no or little treatment resulting in heavy contamination of surface and groundwater in areas having a large concentration of dyeing units as reported in places such as Tiruppur and Pali in India. This contaminated water was unfit for human or animal use and people in the surrounding area had to fetch water from long distances and at huge costs causing them immense hardship. This water was not even fit for irrigating crops, resulting in fertile agricultural land turning barren and farmers being deprived of their livelihoods. It was observed in the study conducted by Rajkumar and Nagan [43] that untreated and partially treated effluent discharged in the river Noyyal by textile dyeing units for the past 20 years has accumulated in the soil and water at many locations and has affected the groundwater, surface-water, soil, fish, and the natural ecosystem in the Tiruppur and downstream area and it would require remedial measures and many years after stoppage of pollution for their restoration. According to the estimates of PWD, Coimbatore, about 25-crore INR would be required for restoring the 40-km stretch of River Noyyal [34]. Thus cheaper synthetic dyes come with huge social and economic and environmental costs.

9 Future Prospects and Conclusion

Brief information about natural dyes, their sources, application procedures, and various advantages and disadvantages of using them was discussed in this chapter. Although many disadvantages such as poor fastness properties and use of banned metal salts and the like can be easily overcome by research and awareness, others such as nonreproducibility of shades and improving the availability would need higher research and industrial investments.

Presently an approximately 1 % share of textiles is only being dyed with natural dyes mostly in the cottage sector by traditional artisans, enthusiasts, and small entrepreneurs. Selling of natural dye-bearing materials and their purified extracts is, however, being done at a small industry level. Many manufacturers in the United States, India, China, and other countries are engaged in this activity and their products are available on the Internet. The tedious application process and nonreproducibility of shades and insufficient availability are some of the factors responsible for their nonadoption in mainstream textile processing. However, at the present level of dye resource availability, their adoption by the textile industry is not desirable also as that would result in an environmental disaster by way of loss of biodiversity and depletion of forest cover in spite of the tremendous environmental advantage offered by them in terms of the lower pollution of the effluent if used properly. This advantage can be utilized by the traditional artisans in preserving their surroundings from the ill effects of pollution caused by synthetic dyes as they do not have access to expensive effluent treatment plants needed for synthetic dyes. A clean production model offered by natural dyes is a better alternative for them. The benefits of research conducted on the development of improved application techniques for better fastness and environmental compliance should reach these people so that they can earn their livelihoods and the consumer also get the benefit of truly environmentally friendly textiles. The availability of natural dyes needs to be increased in a sustainable manner by utilizing the by-products and wastes from agriculture and agroprocessing industries and judicious collection of forest produce. This may be supplemented by growing important dye-bearing plants on wastelands and marginal lands thus providing an alternative cash crop to cultivators. Establishment of proper characterization and certification protocols for natural dyes would definitely improve consumer confidence in natural dyed textiles and would benefit both producers and users. If natural dye availability can be increased by the above-described measures and the cost of purified dyes can be brought down with a proper certification mechanism, there is a huge scope for adoption of these dyes by small-scale dyeing units as they lack the resources to install and operate expensive effluent treatment plants needed to bring the synthetic dye effluent within the limits set by regulatory authorities. If at any time in the future, the availability of natural dyes can be increased to very high levels by biotechnological interventions such as tissue culture or genetic engineering resulting in mass production of these dyes by microbes at low cost, then only can their usage become sustainable for mainstream textile processing. At the level where scientific developments stand today, natural dyes are a sustainable option only for small-scale applications and they can complement synthetic dyes as an eco-friendly option for the environment-conscious consumer and a means of providing livelihood to various stakeholders of the natural dye value chain.

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Sustainable Dyeing with Synthetic Dyes

Martin Bide

Abstract Dyers used skill and logic when they abandoned natural dyes in favor of synthetic dyes. Synthetic dyes were more reliable in strength and shade, did not contain insoluble impurities, or generate spent waste materials that required disposal. They largely avoided the need for mordants, and provided fast bright shades and, for the first time, fast black colors. They could be mixed to allow accurate color matching, and were applied in simpler processes that used far less water and energy. Synthetic dyes have continued to dominate the coloration of textiles while the volume of fiber used each year is now 25 times larger, of which 60 % or more is synthetic. Concern for the environment led to an examination of dyes and dyeing processes: a few synthetic dyes of potential toxicity were earmarked, and have subsequently disappeared from any dyehouse behaving responsibly, and that wishes to do business with major retailers. Recently, 'sustainability' and the erroneous assumptions that natural = harmless, and synthetic = toxic has prompted a voluminous research literature that (re)examines natural dyes. The literature ignores the factors that led originally to their abandonment. In addition, natural dyes cannot produce the amount of colorant required to dye the amounts of fiber produced each year. In contrast, synthetic dyes of all classes and the processes used to apply them become ever more efficient and clean, and offer safe and cost-effective coloration for the world's textiles.

Keywords Synthetic dyes · Natural dyes · Sustainability · Dyeing

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1 Introduction

The origins of sustainability are often seen as emerging from the Brundtland Report of 1987 [1]. However, other than in the broadest terms, there is no common definition of what is sustainable, and the regularly updated "Living Planet Report" [2] makes it clear that we currently "spend" around 1.8 times the earth's capacity each year. What is regarded as "sustainable" on a small scale is unlikely to be effective globally in providing a long-term blueprint for a planet of several billion inhabitants [3]. A case in point is organic cotton, which is widely deemed to be "sustainable." Organic cotton avoids the use of the large amounts of herbicide, pesticide, and synthetic fertilizers required for growing cotton conventionally. A farmer can grow organic cotton year after year and avoid those chemical inputs. However, organic farming is incapable of meeting the current global demand for some 25 million tons of cotton fiber each year: there is simply not enough natural fertilizer, or land available. Therefore, although the organic cotton farmer is seen as "sustainable," that sustainability is available only to a small elite.

The wide-ranging considerations of global sustainability are usually distilled into simpler environmental, ethical, and economic aspects ("planet, people, profit"). Even then, most attention is paid to the environmental part of this trio, and within that narrower scope, the elimination of chemical compounds perceived, however erroneously, as "toxic" is often taken to represent a significant step towards some ultimate sustainability.

Basic human needs are food, shelter, and clothing. Food is usually consumed quickly, shelter is of limited mobility, but textiles both move (and are in contact with the body) and require flexibility (i.e., comfort) and durability. In human history, the important role of textiles was reflected in their high value, and in that many technological advances were applied first to textiles; most notably, the Industrial Revolution was first about mechanizing textile production.

The textile/apparel supply chain begins with fiber production (the agricultural production of natural fibers, or the chemical processing that leads to manufactured fibers). These are then subjected to spinning, weaving, knitting, preparation, dyeing, printing, and/or finishing, and the finished fabric is then cut and sewn into garments. After distribution and merchandising, these are sold to the consumer who wears, washes, and dries them, and ultimately disposes of the worn garment, typically to a landfill. All these steps have impacts on global sustainability. The production of natural fibers involves agricultural inputs that may have sustainability impacts, and, for example, the arguments about the relative merits of conventional cotton, organic cotton, "better" cotton, and GM cotton could fill a book. Lifecycle analyses can offer useful insights into sustainability, but the complexity of textile production is reflected in the corresponding complexity of the LCA of a single fiber, cotton [4].

Today, the textile supply chain deals with more than 80 million tons of fiber per year. Of this, the majority (80 % or so) consists of polyester and cotton [5]. Although cotton is the most widely used apparel fiber, since about 2000 polyester has been the most widely produced textile fiber, and its dominance is projected to increase in the coming years. Fibers differ in the environmental impact of their use and end-of-life disposal, but within the primary textile industry (turning fibers into finished fabric) the major impact is in the wet processes that center on coloration. Humankind sees and appreciates color, and “color sells.” So it is often true that sustainability and textile production meet in the dyehouse.

2 Textiles, Dyeing, and the First Synthetic Dyes

Textiles have been colored as long as they have been produced. Pigments are of limited use on textile materials, requiring some binder that tends to stiffen the fabric, so colorants (dyes) that will color without compromising the tactile nature of the material have been chosen. Pigments tend to have greater fastness and can satisfactorily be used in most nontextile applications. Dyes and textiles thus have a high degree of mutual inclusivity. Colored (mostly organic) compounds have been retrieved from plants and insects and examined for use in dyeing fiber-based materials. Because these materials have evolved for other reasons, their suitability for textile dyeing varies. The subject of natural dyes and dyeing over the centuries has been widely examined [6, 7]. The best of the natural dyes were recognized centuries ago, and the secrets of obtaining bright fast colors were often jealously guarded. More widely available inferior colorants were used by the less skilled, and the distinction was recognized, for example, in the “grand teint” versus “petit teint” dyers.

The value of good dyes was recognized by their importance in trade: the world was scoured for better products. In Europe: cochineal replaced kermes, indigo replaced woad, and quercitron was a valuable addition to weld. The application of these dyes required great skill on the part of the dyers that used them, and it is notable that almost a century passed between the mechanization of textile production and the early synthetic dyes: in that time, natural dyes were used on an industrial scale, aided by the infant inorganic chemical industry that supplied bleaches, acids, and mordants. It was recognized early in this process that chemistry was a valuable tool in the dyer’s arsenal: on the frontispiece of a 1790 textbook is the lament “Tis a pity so few chemists are dyers, and so few dyers chemists” [8].

It should be recognized, however, that although this was on an industrial scale, the world population in 1800 was around 1 billion people, and that the annual fiber consumption was around 5 lb per person per year; that is, global textile production was about 2.5 million tons, less than 1/30 of what it is today.

The story of the first synthetic dye is well known [9]. The concept of a new technology (in this case, industrial organic chemistry) being applied first to textiles again rings true. The subsequent explosive growth of the synthetic dye industry is also well known [10], and synthetic dyes had largely replaced natural dyes by the early twentieth century.

3 Why Did Synthetic Dyes Take Over?

Synthetic dyes readily took over from their naturally derived counterparts for a number of reasons; some were recognized immediately, others became obvious later.

3.1 Synthetic Dyes Produced Colors that Natural Dyes Could Not

This is the reason most often quoted. The corollary of this is that any shade that could be obtained with natural dyes could ultimately be achieved with synthetic dyes, but the reverse is not true.

Interestingly, and not usually recognized, is that a fast black is difficult to achieve with natural dyes, particularly on cellulosic fibers: logwood (typically on a chrome mordant) fades, and a “chemical black” (iron and tannic acid) tends to weaken the fiber. Aniline black, and later, sulfur and direct black dyes were readily adopted.

3.2 Synthetic Dyes Were Free of Insoluble Impurities?

As agricultural products, natural dyes were either supplied as the raw material (roots, wood, etc.) or, in the case of indigo, were extracted at the source: either way, it was difficult to create a solution or suspension free of insoluble material. This was a major problem especially noted in printing, where fine engravings in copper rollers would be clogged. Thus even when good natural dyes were available, most notably madder and indigo, dyers (and printers) readily turned to the purer, grit- and wood-free synthetic versions. At the same time, dyers freed themselves of the grinding, rasping, and crushing required to turn raw material into something usable in a dyebath, and no longer needed to dispose of the waste material from which the dye had been extracted.

3.3 Synthetic Dyes Were Consistent in Shade and Strength

Synthetic dyes were consistent in shade and strength, with none of the variation inherent in a product that comes to the dyer as a small percentage of an (easily adulterated) agricultural product. Dyemakers were readily able to standardize their products so that dyers were able to reproduce shades with little need to carry out test dyeings to determine dye strength and shade.

3.4 Single Dyeing Process

For a given class of synthetic dyes, dyes of different colors can be mixed in a single dyeing process to provide specific colors. This is not usually possible with natural dyes, especially when a primary color is only available from one dye with a unique means of application. Thus indigo was the only practicable natural blue dye, but its application from a bath of leuco-indigo was incompatible with the application of other dyes/colors: these were necessarily applied in a separate process.

3.5 Synthetic Dyes are More Water- and Energy-Efficient

As pointed out in Sect. 3.4, compound shades would often need separate processes for each dye. In addition, using a natural fermentation to reduce indigo might take several days [11]. The “classic” Turkey Red process might take 15 or more separate stages, each of which required a separate bath, over a period of weeks. A straightforward madder red requires maceration in “oily liquor containing sheeps dung” which is repeated several times, steeped in galls (containing tannic acid) and then mordanted, and only then dyed [12]. Even a twentieth-century version might need boiling, oil preparing and stoving, repeated, aluming, chalking, dyeing, second oiling, steaming, and finally two clearings, [13] but the result was apparently worthwhile. A more recent source of natural dyeing recipes suggests a three-step mordant-tanning-mordant sequence: but the weight of chemicals used is as great as the weight of fiber being treated [14]. Such profligate uses of water and energy would be regarded today as highly unsustainable, especially when the results (brightness and fastness) are matched in a much more straightforward dyeing with synthetic dyes.

3.6 Synthetic Dyes Avoided the Need for Mordants?

Use of mordants for dyeing cotton with natural dyes is essential. Natural dyes are most easily applied to wool and silk: most natural dyers and researchers suggesting the use of natural dyes use those fibers, and even then, the use of mordants is required to achieve the best levels of light and wash fastness. Such mordants represent an additional application step, and, beyond iron and aluminum, often mean the use of a hazardous heavy metal.

4 Why Do Synthetic Dyes Continue to Dominate?

Over the course of the twentieth century, the predominance of synthetic dyes was cemented as some of their early limitations were overcome, and additional reasons for their success developed.

4.1 Synthetic Dyes Meet All Fastness Requirements

The fastness deficiencies of early synthetic dyes were overcome as new faster dyes were developed: fast colors were obtained from vat and azoic dyes on cotton with few compromises of color choice. Reactive dyes now provide wash-fast colors in a full range of bright shades.

4.2 Synthetic Dyes Have Low Toxicity

"Toxicity" is an easy charge to lay against a compound, and a difficult one to disprove. For synthetic dyes, "toxic" has almost become a fixed epithet. But the evidence for their toxicity is poor. In many published papers that offer natural dyes as an alternative, "toxicity" is offered as a justification, but rarely is any evidence provided. If a reference is given, it is usually to another natural dye study!

In a sentiment that dates to the fourteenth century, it is said that everything is toxic; it is only the dose that varies (or "the dose makes the poison"). Toxicity may be to acute or chronic exposures, and the latter may be the result not of an original compound, but of its breakdown products.

Synthetic dyes have very low acute oral toxicity. Zollinger [15] refers to a study of 4,461 synthetic dyes. Practically no toxicity was found in 75 % with an LD_{50} of >5 g/kg. Only 1 % had an LD_{50} of <0.25 g/kg. To put these figures in perspective, the sodium chloride that we sprinkle liberally on our food has an LD_{50} of 3–4 g/kg, [16] so the majority of synthetic dyes are less toxic than table salt. A further comparison is that alizarin, the dye component of natural madder, has an LD_{50} of only 0.3 g/kg, [17] almost as toxic as the 1 % of the most acutely toxic synthetic dyes. Very few other natural dyes have been tested. Similar conclusions are drawn by Hunger [18].

Chronic toxicity deriving from long-term exposure shows itself where exposures are highest, and where intermediates (smaller molecules that are more readily absorbed) are handled, that is, in dye manufacture. Exposure in use, in the dyehouse is much lower, and for a dye of good fastness, the exposure to the ultimate user of a colored textile is virtually nil. Early synthetic dye manufacture, in common with many other industrial processes, was ignorant of safety. As the twentieth century progressed, the dangers of the dyemaking processes were recognized, and the hazards of the dyes themselves were reduced by eliminating dyes based on intermediates known to be hazardous, most particularly benzidine and 2-naphthylamine. Other amines of merely possible hazard have since been the subject of elimination, [19] and azo dyes that could possibly degrade into harmful substances now form a part of most of the "restricted substances lists" that are widespread among retailers, apparel producers and their lobbying groups, [20–22] and the specifications for eco-friendliness issued by, for example, Oeko-tex [23]. Other dyes on those lists are those that sensitize. But like the acute toxicity discussed above, the number of dyes affected by such restrictions are a small minority of all the synthetic dyes available.

The recognition that nontoxic and safe synthetic dyes represent an effective way to produce colored textiles is indicated by their inclusion in the Global Organic Textile Standard [24].

The very low toxicity of dyes and dyeing is also revealed in a recent thorough and extensive lifecycle analysis of cotton [4]. The independent study examined the fiber production-to-disposal of woven and knit cotton garments and included measurements of ecotoxicity and human toxicity potentials. The overwhelming majority of toxicity derived from pesticide use in fiber production. Second was the use by the consumer. Virtually no toxicity potential derived from the textile production (including dyeing) steps. This corresponds with early studies of pollution caused by dyeing operations. Such studies looked extensively into the chemicals involved, but any toxicity of effluents was not seen as a result of the presence of dyes [25].

Today, consumer harm from synthetic dyes is practically nonexistent. Meanwhile, the toxicity of natural dyes and the processes used to apply them have gone largely untested.

4.3 Auxiliary Chemicals for Applying Synthetic Dyes Are of Minimal Hazard

Dyes, synthetic and natural, are applied using auxiliary chemicals. Aside from the mordants discussed in Sect. 3.6, a dyer of both natural and synthetic dyes may use salt, leveling agents, pH adjusters, reducing agents, or oxidizing agents. Although large amounts of salt are problematic, processes to minimize its use, or to reuse it are available (see Section Reactive dyes). Leveling agents are typically anionic or nonionic, and of similar composition to domestic detergents. Acids and alkalis are readily neutralized, reducing agents are consumed in the dyeing process, and oxidizing agents are benign. Most dyehouses can, with minimal adjustment, produce an effluent that is treatable in conventional wastewater treatment facilities.

4.4 *Synthetic Dyes Are the Only Practical Choice for Synthetic Fibers*

The twentieth century saw the development of manufactured fibers. Rayon (and later, lyocell) has similar dyeability to the natural cellulosic fibers, and nylon shares dyeability with wool and silk, however, acetate represented a challenge that natural dyes were unable to meet. And the fiber that is now the most widely used, polyester, is similarly undyeable to any significant extent with natural dyes.

5 Why Don't We Go Back to Natural Dyes?

A vast number of research papers in the last 10–20 years have examined the use of natural dyes and offered them as a "sustainable" alternative to synthetic dyes. Despite this, the use of natural dyes on a global scale is extremely small, based mostly on dyes and processes known in the nineteenth century, and it is highly doubtful that any recent research has led to practicable dyeing processes.

5.1 *Natural Dyes Are Water- and Energy-Inefficient*

As Mentioned Above (Sect. 3.5), the Processes Used to Apply Them Tend to be Very Inefficient of Water and Energy Use. Adoption of natural dyes would require greatly increased use of these resources.

5.2 *Natural Dyes Are Applicable to a Minority of Fibers*

Although they work well on wool and silk, these fibers represent only around 1 % of the fiber in use. Cotton accounts for around 35 % of global textile production, for which natural dyes are more challenging (and less efficient) to apply. Wool (and silk) readily takes up metallic salts as mordants, cotton has no such ability and for dyeing, the usual present-day technique involves a lengthy soaking in tannins (which are taken up, albeit inefficiently, by the fiber), followed by mordanting with a metal salt, and then dyeing. The dyeing thus involves three steps, and many hours if not days [7]. Matthews [13] writing in 1921 says "unlike wool… the general class of mordant dyes has but little application to cotton" [26]. In printing, aluminum acetate can be fixed by ageing, the excess removed by dunging, and the fabric then dyed, once again, a three-step process taking long times [27]. O'Neill in his 1869 dictionary's lengthy entry on "fibrous materials" likewise indicates the same ready uptake of colors by wool, and the limited uptake by cotton [28].

Around 45 % of global fiber use is polyester, for which natural dyes are essentially useless (alizarin and unreduced indigo will produce pale shades on polyester).

5.3 Natural Dyes Have No Aesthetic Advantage

“Natural” materials can usefully replace synthetic ones when there is a performance or aesthetic advantage. Natural food often tastes better. Wooden furniture looks better than plastic. But without a sophisticated chemical analysis, the natural or synthetic source of color on a textile cannot be determined.

5.4 Natural Dyes Cannot Meet Global Colorant Demands

In 1850, before synthetic dyes were introduced, and only natural dyes were used, the annual global textile production was around 3 million tons per year. It is currently more than 25 times greater (around 80 million tons). A hectare of land (2.5 acres) will produce around 8 kg of alizarin per year [29]. It was calculated 25 years ago that to dye the world’s fiber with natural dyes would require around 1/3 the world’s agricultural land [30]. Since then, fiber consumption (and thus dye consumption) has continued to grow, so that figure is likely greater today. It would be even greater if it were required that these dyes be produced organically, without the benefit of synthetic fertilizers. The efficiency of natural dye production might be boosted by genetic modification of plants used to produce them, but that would go against the principles of many of those who promote the use of natural dyes. One indicator of the inability of natural dyes to play a significant role in dyeing today is the fact that synthetic dyes are included in the classification of textile materials under the Global Organic textile standard [24]. A further charge laid against synthetic dyes is that they are “oil-based” and that oil will run out. Currently, 90 % or more of the oil extracted is simply burned as fuel. It will last a long time as a chemical feedstock if less of it is simply burned as a fuel. Coal reserves are even greater, and represent a vast resource of organic chemicals, as the “coal-tar” origins of early synthetic dyes makes clear. Ultimately, of course, sustainable chemistry requires the use of renewable sources. Nature produces 130 billion tons of cellulose each year: only 0.2 % of this is used [31]. Investigations of bio-based chemical feedstocks are already under way, [32, 33] and these will ultimately be the source of the large-scale organic chemicals that the world will need, fibers, plastics, pharmaceuticals, and dyes.

6 Using Synthetic Dyes Sustainably

6.1 Sustainability of Dyeing in General

Because, as pointed out in the introduction, what is regularly regarded as sustainable often is not, there is no clear path to follow to achieve long-term sustainability. I may claim to be taking a step down that path by developing a dyeing process that uses 50 % less water and energy, but if I dye twice as much fabric, the planet is ultimately worse off.

Dyeing is, despite its superficial simplicity, a remarkably complex operation that has to consider the form of the material (fiber yarn, fabric), the machinery available, the fastness required, and so on.

Dyeing involves not only dyes, but also adjunct materials both in the dyebath, and in pre- and posttreatments. Dyeing uses water and energy. It is not easy to balance the relative sustainability contribution of, say, the replacement of a material that has an LD_{50} of 250 with a less toxic one of 500, and a process that uses 50 % less water, or 50 % less energy. It is safe to say that of all the recent natural dye research aimed at sustainability, few if any of them, approach the subject from a point of view of water or energy use. At the same time, the attention given to environmental issues means that any new development of dyes, auxiliary chemicals, machinery, or process is framed in terms of its sustainability advantages. Separating real advances from those that are less valid is not always easy.

Much of what is regarded as "sustainable" today springs from the broader societal recognition of pollution and the effects of industry on the environment that occurred in the 1970s. In the United States, the Environmental Protection Agency surveyed the textile industry and identified significant sources of pollution [25]. These surveys showed that little of concern involved the toxicity of the dyes being used.

Initial efforts to mitigate the pollution via end-of-pipe treatments were recognized as expensive and inefficient, so focus shifted towards pollution prevention and the modification of processes, and material substitution to meet ever more stringent standards. As mentioned earlier, in the primary textile industry, most of the impact (chemical, water, energy) occurs in the preparation and dyeing steps, and companies were largely able to meet the requirements with the reduce, reuse, recycle approach [34]. Attention included air emissions (not concerned with dyes) and water discharge. In this latter sphere, limits were usually expressed in terms of pH, BOD and COD, TDS, suspended solids, heavy metals, oil and grease, and color. Although attention to environmental issues undoubtedly played a part in reducing global impact, the changes made were usually in response to very local regulations. Broad principles in making dyeing sustainable were widely recognized [35]. Measurements of effluent toxicity (measured, e.g., on daphnia) tended to reveal that salt and metals were the major culprits, and that once again, dyes presented no other problems beyond their being colored.

As attention has shifted from "pollution" to sustainability, the effect of dyeing is often viewed in one of two ways. The easiest to demonstrate is that the product will not harm the user, or harm the environment in use. A primary example is the Oeko-tex 100 scheme that certifies items being sold as environmentally sound based on what is present or might be released from them [36, 37]. Like the GOTS, this recognizes most synthetic dyes as acceptable, but identifies particular dyes as unacceptable based on their ability to break down into harmful compounds, or their sensitizing nature. The good fastness of most synthetic dyes reduces the exposure.

The second measure of sustainability is based on the environmental impact of the production of the item: in this case, the subject is dyeing, and thus involves the impact of dyeing on the environment. That, therefore, is the subject of what follows.

6.2 Synthetic Dyes Overview

The development of synthetic dyes in the later nineteenth century led to their being grouped in classes of similar application procedure. These later became codified in the Colour Index (originally published through three hard-copy print editions, but now hosted onlnine), [38] and were joined by other classes of dye as they were developed. Thus acid dyes were appropriate for use on wool, silk, and (later) nylon. (Chrome) mordant dyes were used on wool. Direct ("substantive") dyes, sulfur dyes, azoic dyes, and vat dyes were available for dyeing cellulose, joined later by reactive dyes. Acetate required the development of "acetate dyes" and when these were found to be useful on nylon and polyester, were referred to as disperse dyes. Basic dyes, among the earliest of the synthetic dyes, were originally applied to (mordanted) cotton, silk, and wool, but later found wide use in dyeing acrylic fibers.

The remainder of this chapter is devoted to looking at the details of the use of these various classes of synthetic dyes in the light of the context given earlier, that is, that those in use today are safe, and efficiently applied. However, the economic drivers that have forced dyers to examine their operations and adopt the most cost-effective means of getting commercially acceptable results mean that within any given type of dye, or application process, opportunities exist for more efficiency (and thus sustainability). Growing environmental regulations (and the penalties that derive from ignoring them) act as a further spur for greater attention to processes that are inherently more sustainable than those involving natural dyes.

The use of natural dyes, although not contributing in real terms to sustainable objectives, may feed the erroneous beliefs of the ultimate customer who wishes to proclaim a product "green."

6.3 Dyeing Overview

The general theory and practice of the application of dyes to fibers has been extensively covered in many standard sources [39–41]. These cover the different types of dye available, the various fibers to which they can be applied, and the types of machine used for the application at various stages of fabrication from fiber through to garment. The following discussion largely assumes the reader's familiarity with this background. The methods used to do this with minimal environmental impact have also been dealt with in prior publications [42].

Preparation of fibers and fabrics before dyeing is an essential part of a successful dyeing: the old saying is, "Well prepared is half dyed," implying that many of the faults seen in dyed fabrics can be traced back to poor preparation. Because they are agricultural products, the importance of preparation is seen most clearly for cotton and wool and silk. Preparation is equally important before dyeing with natural or with synthetic dyes, so that aspect of textile wet processing is not discussed further.

A dyer should achieve the correct shade and fastness properties on a fabric in a level manner as efficiently and profitably as possible. Each of these can affect the sustainability of the process.

6.3.1 The Right Color

The color that a dyer is trying to use will often be supplied as a standard shade in the form of a colored sample, or a reflectance curve obtained from a spectrophotometer. The electronic communication of color standards and dyed shades has become more common as the textile supply chain has become global.

With synthetic dyes, matching the standard color usually means applying (in a single step) a mixture of three dyes, typically yellow, red, and blue. These will usually be chosen to have similar dyeing behavior and may be supplemented by others to allow particular shades or fastness properties to be achieved, or to reduce metamerism. Of course, cost is an additional factor. In comparison, natural dyes cannot readily meet these broad goals. Especially because indigo is the only practicable blue natural dye, and its application is incompatible with other dyes in the same process, any shade requiring a blue component has to be dyed in two or more stages.

Matching color with synthetic dyes (supplied as well-standardized materials) can be automated in instrumental match prediction, which generates recipes rapidly, minimizes metamerism, and (in a well-controlled dyehouse) can provide high percentages of right first-time dyeing, and even allow for blind dyeing, in which the right shade is assured. Getting the right color in the shortest possible time minimizes energy use, and is a significant contributor to sustainability [43–45]. These systems require that dyes be calibrated ahead of time at known depths of shade, and thus instrumental match prediction is ill-suited for natural dyes. Their inherent variation of strength and shade precludes worthwhile calibration.

The recipe for a dyeing also includes the additives (electrolyte, pH adjustments, leveling agents), the time and temperature profile, and the liquor ratio. These in turn may depend on the details of the machinery in which the dyeing is to take place. The well-known "fishbone" diagram [46] of the variables that can contribute to shade variation demonstrates all that dyers must control: with the variations inherent in natural dyes, and the separate need to control a mordanting step, it is clear that accurate shade control with natural dyes is not easy. With synthetic dyes, dyers can examine a shade at the end of a dyeing process, make an add, and run the process for a while longer to correct the shade. This is not easy to do with natural dyes. Few if any studies have been done on accurate shade matching with natural dyes.

The accurate control of color with synthetic dyes has allowed for highly reproducible dyeings that match the standard closely. That closeness is measured objectively with spectrophotometers and good modern color difference equations such as CMC(l:c) can make pass–fail decisions better than a human observer, and allow for very close control of color. In turn, this leads to efficiencies in the downstream cut-and-sew processes: large lots of fabric can be cut and sewn together, without having sleeves and bodies being noticeably different. Garments from multiple components can be accurately matched and sewn together. All the garments on a rack can be the same color. Natural dyeing processes are difficult to control to the accuracy of color required to do this. One is faced either with the need to make repeated adjustments to a given dyeing (increasing energy and use of machine, and risking damage to the textile) to make it right, or accept that colors from such dyes will vary a great deal more than with synthetic dyes. This may be acceptable for a small "craft" segment of the apparel market, however, it will not provide the well-matched clothes that customers require. Thus the use of natural dyes means that we give that up and accept that garments on a rack, or sleeves and bodies, do not match.

6.3.2 Level Dyeing

A dyeing in which dye is distributed evenly throughout the substrate is referred to as level. Ideally, each fiber should be fully and evenly penetrated, but in practice fibers in the middle of a yarn are often dyed lighter than those on the outside, and there may be pale areas where yarns within a fabric cross each other. These micro-unlevelnesses are generally acceptable, but on a larger scale, any streaks, spots, crease-marks, as well as more gradual and subtle variations from side-to-side, side-to-middle, back-to-front, or end-to-end of a fabric are unacceptable. Dyers of synthetic dyes have many tools that allow them to generate level dyeings. In continuous dyeing, levelness may be achieved from level initial padding of dye (few natural dyes are applicable continuously), or an even initial "strike" in batch (exhaust) dyeing. Conditions (temperature rise, pH, auxiliaries) can be adjusted in batch dyeing to achieve levelness.

Application of synthetic dyes in a one-step process minimizes the risk of unlevelness. Natural dyes tend to suffer more from this fault. An uneven mordanting step will produce an unlevel dyeing, which only becomes apparent when dyeing is carried out, and will be hard to correct. Getting shades from two dyes in two separate processes also increases the risk of unlevelness. The application of indigo is inherently unlevel, and virtue is made of this in the stone-washing processes for denim that rely on abrasion to reveal the undyed white interiors of indigo-dyed warp yarns. Unlevelness may render a material unsaleable, or require reworking which once again consumes additional energy, water and chemicals.

6.3.3 Fastness

A dye that resists removal, or destruction is said to be fast. A colored textile might encounter challenges in both textile processing subsequent to dyeing, or (most likely) in ultimate use. Those challenges might be replicated or approximated in standard laboratory tests that predict their effects. Such tests are developed and maintained by AATCC and ISO among others [47].

Dye selection is the main factor in achieving a fast dyeing. The vast number of synthetic dyes includes many of excellent fastness, and on any given substrate satisfactory fastness is obtainable. The restricted choice of natural dyes limits the fastness that can be achieved. The need for mordants makes processing more complex and less efficient in terms of water and energy use, but mordant–dye complexes often have good fastness, and so within the limited shade range inherent with natural dyes, good fastness may be obtained. A good fast black, however, is difficult with natural dyes, which explains the readiness with which dyers and printers adopted aniline black when it was first developed in the 1860s.

Fastness also depends on the removal of unfixed dye at the end of the dyeing process. This might be accomplished with a simple rinse, or a more severe washing process. Again, natural dyes are less efficient, and after the application of a madder shade on cotton, a boiling with soap was (and is) still required to remove the stain of unmordanted dye, especially in printed fabrics where white areas must be free of such stain.

6.3.4 Efficiency and Sustainability

As should be apparent from the above, synthetic dyes are applied in highly efficient processes. Success requires achieving the correct shade, applied in a level manner, with the appropriate fastness. This must be done while making best use of chemicals, water, energy, labor, and machinery; only then can a dyer make a profit. The processes for the application of synthetic dyes are typically one step, with no need for prior mordanting. Natural dyes often require mordanting, and may even then require more than one dyeing step to achieve the required shade. They thus require considerably more water and energy to apply them, making them less sustainable. The customers for natural dyed products must also “make do” with the limited range of shades, lack of fastness in some colors, and limited reproducibility of colors.

6.4 Specific Dyeing Processes

The next section covers textile fibers and the advances made in the sustainable dyeing of them. As pointed out, the first iterations of these dyes and the processes used to apply them were inherently more sustainable than the natural dyes they replaced.

6.4.1 Dyeing Cellulose

Cotton is by far the most widely used cellulosic fiber, but for dyeing operations, most of what applies to cotton applies to other natural (linen, hemp, ramie, etc.) and regenerated cellulose fibers such as viscose rayon, high wet modulus rayon (modal, polynosic), and lyocell fibers.

Cellulose is a hydrophilic fiber, and requires hydrophilic dyes. Hydrophilic dyes, if they remain as such, will retain an affinity for any aqueous environment, particularly that found in laundering. Cellulose fibers are typically robust and can withstand aggressive laundering conditions. The history of dyeing cotton has thus been a search for good fastness to wet conditions. A few natural dyes could achieve this: reaction with a mordant might generate a dye–mordant complex of low solubility (and thus higher fastness). Thus Turkey Red dyeings of madder on an aluminum mordant would have good wet fastness. Cochineal, despite its ability to produce bright shades, cannot do so: the carboxylic acid in the structure of carminic acid renders its mordant complexes too soluble, and it cannot withstand the rigors of laundering. For red colors, madder is usual on cotton, and rarely applied to wool (the brown impurities dye the fiber and dull the shades), whereas the reverse is true for cochineal: [48]. Matthews indicates, “cochineal has no application on cotton” [49].

Indigo (or the chemically identical woad) achieves its wet fastness via a reversible solubilization sequence. The initially insoluble colorant is made soluble by reduction. Originally a (slow, smelly) fermentation would do this. Later, as the inorganic chemical industry developed, lime/ferrous sulfate (“copperas”), orpiment (arsenic sulfide) and zinc/bisulfite systems were used to reduce indigo. Ultimately hydrosulfite became most widely adopted; today, electrochemical methods, or thiourea dioxide are also available, the former requiring much reduced chemical inputs. The indigo may be “natural”; it is a matter of debate how natural are the chemical reducing agents used to dye it, versus a fermentation-based reduction. After dyeing, the dye is oxidized by air to its original insoluble form. The insolubility provides good wet fastness.

Dye exhaustion is generally lower on cellulose fibers than on other fiber types, and thus waste streams are more highly colored. The greater exhaustion of dye on protein fibers was noted centuries ago, and in the nineteenth century, processes for "animalizing" cotton were researched, resulting in the application of protein materials such as albumin, lactarine, and the like to the fiber [50]. These efforts have continued in various forms in the years since, and the most recent incarnation has been the development of "cationic cotton" within which are positively charged groups to which anionic dyes are attracted with high exhaustion and minimal use of electrolyte [51–54]. These are produced commercially, and the use of this fiber with natural dyes is currently being researched [55].

Synthetic dye development for cellulosic fibers, although producing simpler processes and a broader range of colors than can natural dyes, has done so while meeting many of the requirements for good wet fastness.

Direct Dyes

Direct dyes were originally known as "substantive" dyes, reflecting their ability to dye cotton without the need for a mordant. Substantivity for cotton is rare in natural dyes (annatto and turmeric are exceptions, although they have other major limitations that preclude any wide use) and the ability to produce dyeings in a straightforward operation made direct dyes immediately popular following the introduction of the first one (Congo Red) in 1884. Salt (sodium chloride or sodium sulfate) is used to promote exhaustion by neutralizing the positive charge on the cotton surface that would otherwise repel the anionic dyes. The simplicity of operations, involving no chemical change in the process, has the downside of a limited fastness to wet treatments. Later developments sought to answer the deficiencies of fastness with postmordanting with copper salts, treatment with formaldehyde, and (most successfully) a diazotization and development sequence applied to the dyed fabric that resulted in excellent wet fastness properties at the expense of the additional step.

In terms of sustainability, these dyes epitomize the kinds of change that have taken place in synthetic dyes generally. Early ones were readily adopted, albeit with fastness limitations. These were answered initially with posttreatments that are environmentally questionable or make the operation less efficient. Ultimately, better dyes were developed to re-establish the simplicity and achieve fastness at the same time. Meanwhile, the chemistry of many of the early direct dyes was based on compounds (most specifically benzidine) later recognized as carcinogenic. Continued research has provided dyes that still meet the requirements, but with chemistry that avoids those earlier dangers [19, 56]. With no chemical change in the process, the baths used for dyeing direct dyes can be recycled [57, 58]. For dark colors, especially blacks, a standing bath can minimize the amount of wasted dye. Their use has declined with the development of reactive dyes.

Sulfur Dyes

Sulfur dyes have their origins in “Cachou de Laval” a brown dye derived from sawdust in 1874, but which only became popular after the introduction of sulfur black T in 1896. The principle of a well-defined organic starting material being treated with sulfur and/or sulfides to produce colored dyes has led to a wide range of commercial products characterized by good fastness (considerably better than that of direct dyes), and low price. The dyeing process is similar to that for vat dyes, with dye being applied in a reduced form, and later oxidized to an insoluble (and thus fast) colorant on the fiber. A contrast is that sulfur dyes are usually supplied in prereduced form: the leuco compounds are more stable than the vat dye leuco compounds. The shades they produce are typically dull, and a common use for sulfur-dyed material would be work wear. Once again, the early dyes represented an advance of simplicity and color range over natural dyes, and as time has passed, developments have refined both the dyes and their application to better meet the demands of sustainability. Sulfides are used in their production (and thus present in the dye as sold), are polluting, and dyemakers have minimized the free sulfide present in the dye. Alternative reducing agents for use in the dyebath, such as glucose, have minimized the sulfide present in effluent [59, 60]. As with vat dyes, the use of electrochemical reduction has been explored [61]. Oxidation of sulfur dyes was formerly sometimes carried out with polluting dichromate, but when air (or the oxygen contained in rinsewater) is insufficient, benign alternatives are now available [62].

Vat Dyes

Indigo was the prototype vat dye, and all dyes of this class follow the indigo model of reduction to a soluble leuco compound by “vatting” with a reducing agent, application to the fiber, and subsequent reoxidation to the original insoluble form: the lack of solubility and the formation of molecular aggregates (essentially pigment particles) gives these dyes superlative fastness. The ubiquity of indigo led to the extensive research into its manufacture synthetically, and commercial synthetic indigo was on the market by 1892. The broader class of vat dyes has its origins in subsequent research into analogues of indigo that provided (somewhat fortuitously) the dye “Indanthrene” in 1905. Since then, many more such vat dyes have been introduced, most of which have much better dyeing properties than indigo in that the exhaustion is much greater and dark shades can be dyed directly without the need (as in indigo) to perform multiple dip/reoxidize sequences. Indigo today is thus an outlier, and it might be argued that if indigo did not exist, and it was to be invented today, that its properties would be regarded as highly unsatisfactory!

In sustainability terms, vat dyes exhaust well and thus lead to minimal dye discharged into the environment. The reaction products of the reducing agent used in their application, most commonly sodium dithionite (hydrosulfite), may be eliminated by the use of alternative reducing agents [63]: most recently electrochemical reduction has been explored and offered on a commercial scale [64, 65]. Chemical oxidizing agents to bring the dye to its final oxidized form can be replaced by exposure to air. The ability to provide such excellent fastness contributes to the longevity of items in use, and delays the need for replacement and the environmental impact of producing it. The manufacture of vat dyes requires a multiple-step process, and was among the less efficient and more polluting ones. Once more, subsequent research has eliminated dyes shown to be harmful, and has provided cleaner processes for making others.

Azoic Dyes

Azoic dyes are created on the fiber itself. In effect, the dyer is the dyemaker. A coupling component (a "naphthol") is applied first, and the fabric then treated with a diazonium salt produced by diazotizing a "fast base": the diazotization reaction is carried out at cool temperatures, and these dyes are thus referred to occasionally as "ice colors". The first azoic dye was Vacanceine Red introduced in 1880. Fabric padded with 2-naphthol was passed into a bath of diazotized 2-naphthylamine, and an insoluble red azo dye was created in situ. Once again, insolubility means good wet fastness, and later developments, particularly para red was a ready rival for Turkey Red, offering comparable fastness and brightness in a much simpler process.

The applicability of azoic dyes was improved in 1912 with the introduction of the first naphthol (Naphthol AS) with substantivity for cellulose fibers, allowing for exhaust application. Different naphthols and different fast bases provided many combinations but azoic dyes are strongest in the red and burgundy shades, with navy and black also being useful. They formed a useful complement to the vat dyes, with comparable fastness, and providing colors that were more difficult to obtain with vat colors. As the twentieth century progressed, research led to prediazotized fast bases (sold as "fast salts") and stable premixed combinations of naphthol and fast salt that could be applied in printing with the reaction occurring on subsequent steaming with acetic acid present. Of all the dye classes for cellulose, azoic dyes are the least widely used today, having been superseded by the reactive dyes to an even greater extent than the direct dyes.

Reactive Dyes

Reactive dyes are the most recent new class of dye, introduced originally in 1956 They are applied to the fiber much as is a direct dye (in batch dyeing, exhaustion is promoted by the addition of electrolyte) but the dye contains a functional group (or groups) and in the later stages of the dyeing the addition of alkali causes a reaction to take place between dye and fiber. The resulting covalent bond produces good fastness to wet treatments, and the simplicity of the dye structure allows for a full gamut of bright shades to be produced. A combination of simple application, straightforward chemistry (most are based on azo), bright shades, and good fastness has meant that these dyes have become the default choice for dyeing cellulose. The broad shade range and good wet fastness of reactive dyes means that direct dyes are used far less often than before. Bright red reactive dyes have rendered azoic dyes almost obsolete, and black reactive dyes challenge the former widespread use of sulfur dyes for that color. Except for end uses that require high fastness to light, where vat dyes still enjoy an advantage, reactive dyes are ubiquitous.

In the 60 or so years since their introduction, they have been subject to extensive research and development. Earlier work by companies other than the originators was aimed at getting to market and not infringing patents, and so a large number of different reactive functional groups were explored. As patents expired, the market largely defaulted to halogeno-triazine and vinyl sulfone reactive groups.

The early reactive dyes exhausted poorly, required a lot of salt in their application, and the inefficiency of the reaction with cotton left a large amount of unfixed, hydrolyzed dye to be removed by extensive rinsing after dyeing. Dyemakers have worked hard to overcome these limitations to make reactive dyes highly sustainable. High fixation efficiencies can be achieved via the use of two or more reactive groups of the same (homo-) or different (heterobifunctional) types. Molecules with higher substantivity have better exhaustion with lower amounts of salt: so-called “low salt” dyes are among the most efficient [66, 67]. These dyes are also highly suited to application by continuous and especially semicontinuous (pad-batch) processes, where salt can be omitted completely, and reaction efficiencies are high, resulting in a far less intensive rinsing step [68]. Efficient rinsing processes have been studied [69] and enzymatic processes for decolorizing the rinsewater have been developed [70]. The salt from decolored dyebaths can be reused [71].

6.4.2 Dyeing Wool and Silk

Wool and silk are the two other major fibers for which it is possible to look back at natural dye applications and compare the sustainability of those processes with those for the application of synthetic dyes, both when synthetic dyes were first introduced, and more recently as synthetic dye developments have answered lingering questions of sustainability.

Dye application (whether natural or synthetic) on protein fibers is generally more straightforward than on cellulose fibers: the fibers are replete with functional groups capable of binding with dyes, and almost any colored substance will at least stain them. It is for this reason that the vast majority of natural dye application, be it by craft dyers, small-scale commercial dyers, or by researchers examining potential new sources of natural dye, is on wool and silk, despite the limited commercial significance of wool (around 1 % of the world’s fiber each year) and even less of silk (around 0.1 % or less). The comments below concentrate on wool, but apply equally to silk.

Dyers recognized very early on that even though many natural dyes would exhaust well, the fastness, particularly to light, was poor, and could be improved by mordanting the wool prior to dyeing. Aluminum, tin, and iron were commonly used, supplemented with chrome when that became available in the early nineteenth century. The color gamut of a limited number of satisfactory natural dyes could thus be extended by use of different mordants.

Synthetic dyes similarly found ready application on this very receptive fiber. Simple anionic dyes were applied with the assistance of acid (and thus became known as "acid dyes") and the better fastness of mordant-assisted dyeing was reflected in a growing number of synthetic dyes with groups capable of chelating with metal, thus mimicking the natural mordant dyes. The range of shades was extended with new dyes, rather than with using different mordants, and very soon chrome became the mordant of choice. Mordant dyeing of wool with synthetic dyes in the early twentieth century was thus of similar sustainability to natural mordant dyeing, and when premordanting was superseded by afterchroming, became a more efficient process, and allowed the economical production of fast dark colors on wool. Challenges of environmental sustainability more recently led to extensive research into minimizing the amount of chrome wasted, or the form in which chrome is discharged [72–74].

Meanwhile, acid dyes were under continuous development, and dyes of better fastness (so-called milling and supermilling dyes) were able to provide bright colors and fastness for most end uses with no need for metal mordants. The exhaustion of dyes on wool is high, and what auxiliaries are used to promote levelness are present at low concentrations. Minimal rinsing after dyeing is required. Synthetic acid dyes thus represent a highly sustainable dyeing system for wool. In the mid twentieth century 1:1 and later 2:1 metal complex dyes were developed and may be seen as the start of a movement away from chrome mordant dyes. These dyes provided high fastness, and because the metal atom is chelated within the dye molecule, the very small amounts of dye left in the exhausted bath contain metal with little or no bioavailability. The use of the environmentally benign iron as an alternative to chrome in metal complex dyes has been examined [75, 76].

Reactive dyes for wool were originally explored as a way to get good fastness and bright shades on shrinkproof (machine washable) wool. These also offer a metal-free way of getting the best fastness in dark colors [77].

6.4.3 Dyeing Nylon

Like wool, nylon is most often dyed with acid dyes, and the issues surrounding its dyeing are largely the same as those described above for the dyeing of wool. The exception is chrome mordant dyes, which have rarely been used on nylon. Routinely 2:1 metal complex dyes are used for dark colors, and the issues involving the metal content of premetallized dyes are the same. Nylon is a more robust fiber that wool, and has greater fastness challenges, so fastness is of concern and postdyeing treatments to improve fastness are common. Backtanning processes (involving antimony salts) were used, but have largely been replaced by the more environmentally acceptable "syntans." Modified aftertreatments, and nonantimony tanning systems have been examined [78, 79]. The use of alternatives to acid dyes, such as sulfur dyes, vat dyes, and reactive dyes have been suggested as ways to improve fastness [80, 81].

6.4.4 Dyeing with Disperse Dyes: Polyester and Acetate

The sustainability issues here cannot be compared to those involving natural dyes inasmuch as the fibers were developed when natural dyes had already become an historical curiosity. The ability of natural dyes to color these fibers is limited, and does not offer a practical solution to their routine coloration. Polyester is now the most widely used fiber in the world, so its sustainable coloration is important.

Disperse dyes were developed first for use on acetate that was introduced as a new fiber in the 1920s. When polyester was introduced in 1950 the same dyes were found to be useful, albeit with some limitations in application and fastness. The diffusion of disperse dyes into polyester at boiling temperatures is slow, and the limited number of dyes that would diffuse quickly enough had poor fastness to heat treatments: they would sublime. Until this time there had been no need for dyeing machines to be pressurized to achieve temperatures above 100 °C, and these were unavailable when polyester was introduced. Successful dyeing thus required the use of chemicals that would penetrate the fiber and lower its glass transition temperature: these became known as carriers. They were mostly aromatic hydrocarbons, phenols, or chlorinated aromatics, were used at quite high concentrations and ended up as pollutants in the wastestream or volatilized into the air. Pressurized dyeing machines allow ready diffusion of dye into polyester without such carriers, and as the production of polyester has grown, such machines have become the norm. They additionally offer faster dyeing cycles. At the same time, newer disperse dyes specifically for polyester were eventually developed. For fabrics (polyester–wool blends, most notably) more benign migration assistants allow for dyeing to take place at lower temperatures and have replaced many of the questionable chemicals used as carriers.

When dyeing polyester in dark shades, the low aqueous solubility of disperse dyes may lead to the presence of surface dye and cause poor rubbing fastness. This is traditionally removed in a "reduction clearing" process with dithionite and alkali, with the same environmental question marks as apply to their use in the application of vat dyes. Dyes clearable with an alkali treatment have been developed [82]. In most polyester dyeing processes, a pH of 5–6 is maintained with acetic acid for dye stability. Recent interest has focused on the selection and use of dyes stable in alkaline baths which reduces the need for reduction clearing [83–85].

The application of dyes from nonaqueous solvents was studied in the 1970s but resulted in few commercial applications and the most common solvent suggested cannot be considered sustainable. More recently, however, dye application from supercritical CO_2 has been investigated. This is suitable only for nonpolar dyes such as disperse dyes and this has now become commercial practice on a large scale [86].

The dyeing of polyester is probably the most sustainable coloration process of all. Very few auxiliaries are required, the exhaustion is high, so the spent dyebath contains only the dispersing agents that are used in dye manufacture (and these are often derived from the lignin waste from paper making) and so is readily dischargeable (or better, recycled). The fastness of the resulting dyeing is, with appropriate dye choice, excellent. The dyes do not contain metals.

6.4.5 Dyeing Acrylic Fibers

Like polyester, the dyeing of acrylic fibers has no natural dyeing process with which to compare its sustainability. Early acrylic fibers were difficult to dye, or dyeable with acid dyes. More successful acrylic fibers were developed, dyeable with basic dyes, many of them the same classic dyes developed in the early days of synthetic colorants (Malchite Green, Methylene Blue, and so on). These were later supplemented and ultimately replaced with "modified basic dyes" synthesized specifically for use on acrylic fibers: many of them were simple modifications of disperse dyes for polyester. The dyeing of acrylic fibers presents few specific environmental challenges beyond those discussed previously. Dyes exhaust well. Levelness can be challenging, which tends to increase the use of leveling agents. Both factors would make dyebath reuse an attractive proposition.

6.4.6 Dyeing Blends

When natural dyes were still in common use, the only blends of differently dyeable fibers were those based on cotton and wool. A fabric of cotton warps and wool wefts (a "mouselline delaine" or more simply a "delaine") would be dyed or printed using methods appropriate for wool [48]: as discussed above; this was the more readily dyeable of the two, and wool might suffer from the more robust conditions that cotton treatments require.

With the wide range of regenerated and synthetic fibers now complementing the natural fibers, designers can produce many different blends for both technical and economic reasons, and many different blends are encountered. When these are dyed, the dyer may need to dye them both the same color, keep one of them white, or dye them two different colors. The subject has been extensively covered [87].

The same principles of sustainability as for single-fiber fabrics apply, and synthetic dyes can accomplish what is required in an efficient manner. An elegant example would be the dyeing of a wool–cotton blend with a reactive dye, where the hydrolyzed reactive dye exhausts onto wool as an acid dye [88].

Where one of the fibers is a synthetic, the ability of natural dyes is severely limited. Cotton and polyester together make up around 80 % of all fiber consumption, therefore a blend of the two is probably the most common. Such a blend can readily be dyed in a two-bath two-step process (somewhat akin to the processes used to apply natural dyes to a single fiber!), but research efforts have developed more efficient one-bath, two-stage, or even a one-bath one-stage process, with concomitant savings in water and energy, and improved sustainability [89–92]. In continuous dyeing similar research has been published [93].

7 Conclusions

A dyer wishing to produce colored fabrics sustainably can do so best by the use of safe and efficient synthetic dyes. Such dyes (and the processes used to apply them) resulted in much lower environmental impacts than those using natural dyes. The dyes are safe, mordants are not required, and the processes use far less water and energy than natural dye application. The dyes also meet the global organic textile standards. They achieve faster shades in a wider range of colors than natural dyes.

The application of natural dyes, when they were all that was available, represented a triumph of ingenuity and chemical skill to produce useful dyeings from materials not designed for the purpose. One can look back and appreciate that skill, and perhaps keep it alive in the same way that other ancient skills are. But as a practical and clean way to provide the immense volume of colored textiles that the more than 7 billion people on the planet require, they have no real use.

As environmental impacts and sustainability have come to the fore, synthetic dyes and the processes and machines used to apply them have continued to evolve. Reduced water and energy consumption bring economic as well as environmental benefits. The few chemicals used (salt, leveling agents, etc.) are benign and are mostly used at low levels. More advanced methods for reducing the environmental burden of dyeing such as dyebath reuse, or dyeing from supercritical CO_2, have been tested on a commercial scale.

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

Sohel Rana, Subramani Pichandi, Shama Parveen and Raul Fangueiro

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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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]

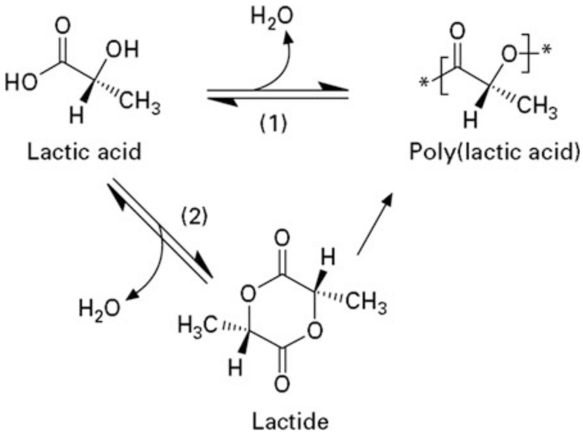


Fig. 2 Stereo isomers of lactic acid [29]

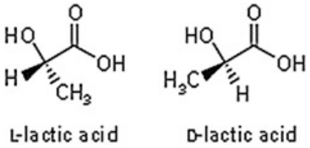
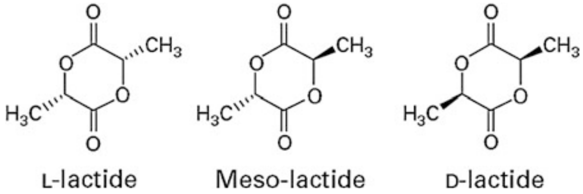


Fig. 3 Dimeric lactide isomers [29]



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.

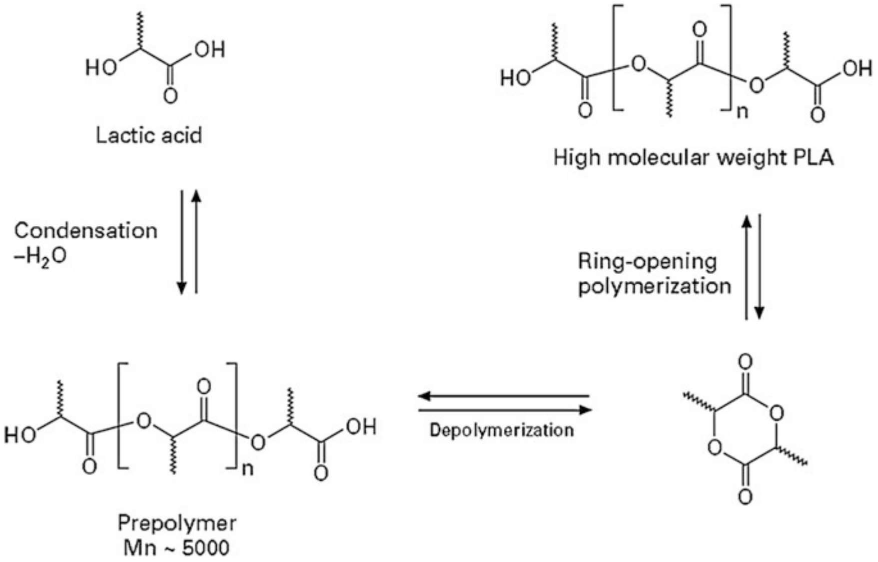


Fig. 4 Production of high molecular weight PLA via prepolymer and lactide formations [29]

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.

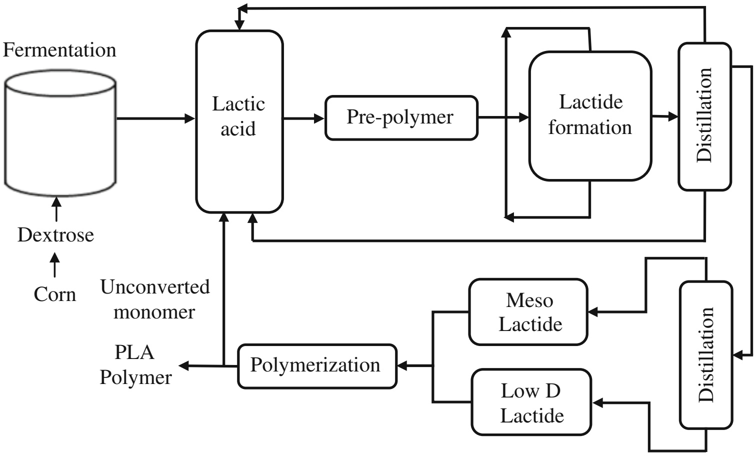


Fig. 5 Nonsolvent process to prepare polylactic acid [29]

- 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.

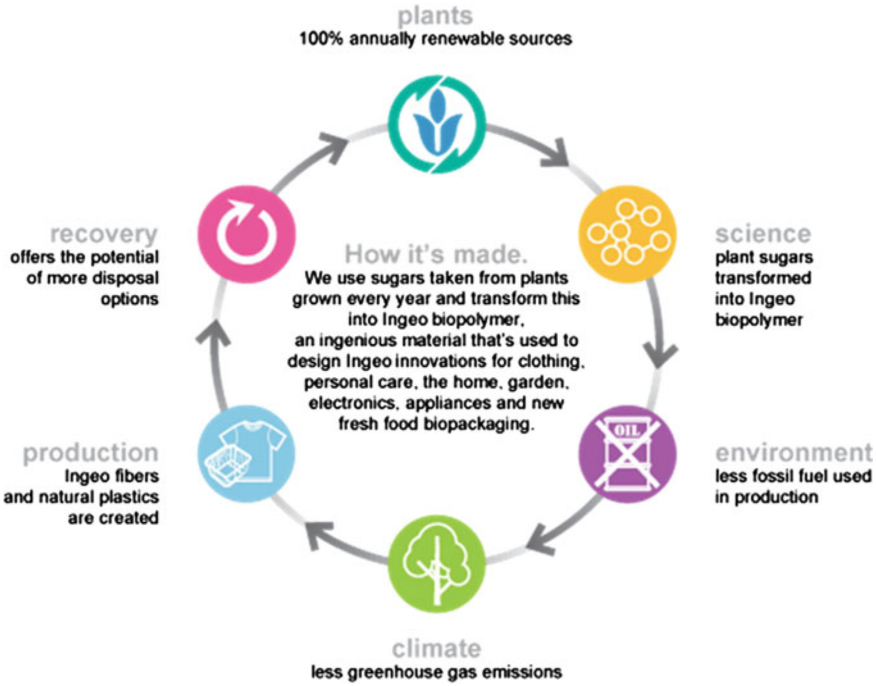


Fig. 6 PLA lifecycle [32]

- **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.

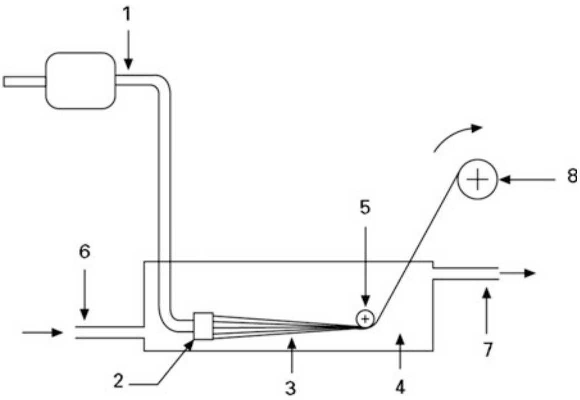


Fig. 7 Schematic diagram of a horizontal wet-spinning system. *1* Inlet of the spinning dope; *2* Spinneret; *3* Spinning line; *4* Coagulation bath; *5* Take-up godet; *6* and *7*. Inlet and outlet of the spinning bath [26]

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

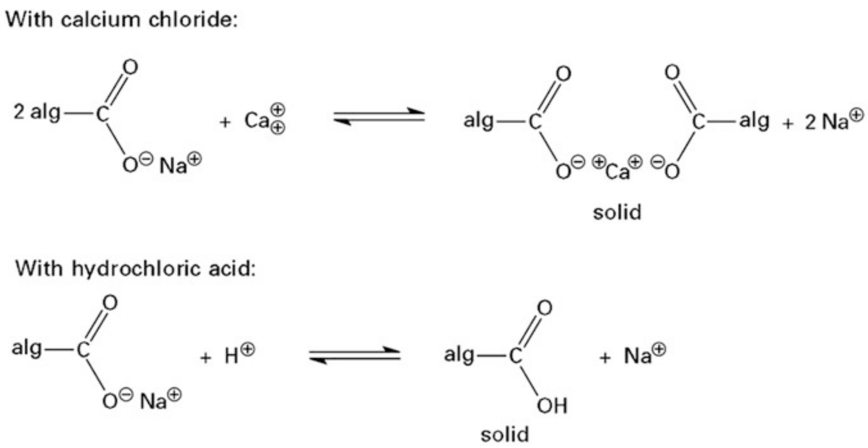


Fig. 8 Chemical reactions in coagulation process [26]

- 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].

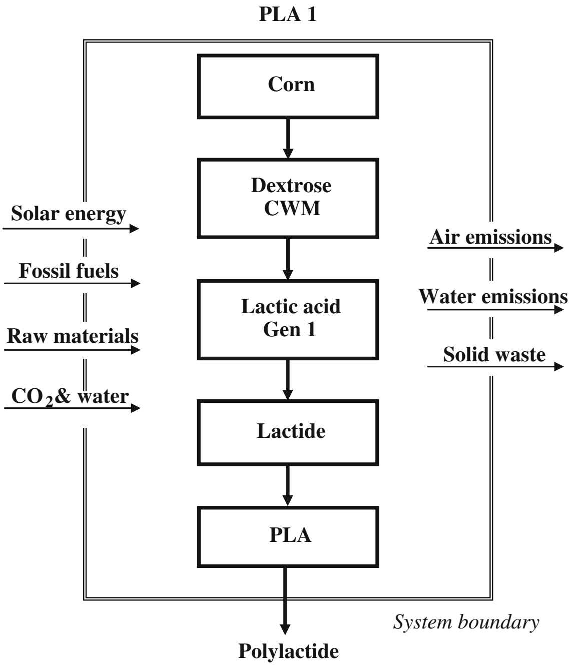


Fig. 9 System boundary for PLA1 process [38]

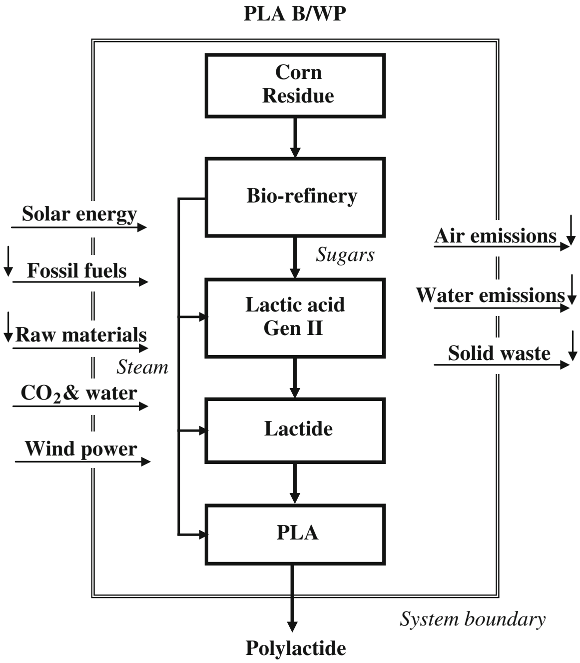


Fig. 10 Systems boundary for PLA production with biomass feedstock and wind energy input [38]

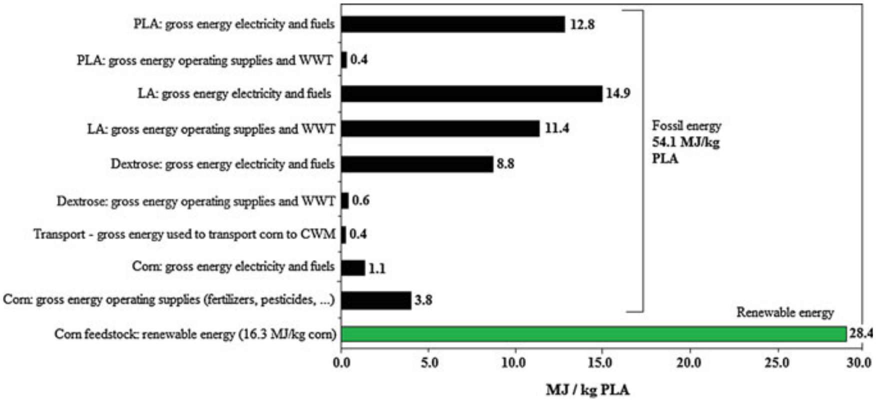


Fig. 11 Contributions to the gross energy requirement for PLA1 process [38]

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].

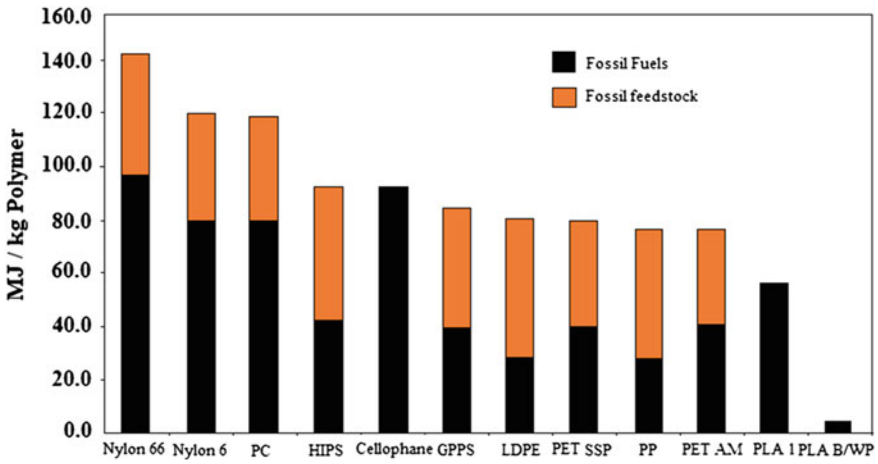


Fig. 12 Fossil energy requirement for some petroleum-based polymers and PLA. The cross-hashed part of the bars represents the fossil energy used as chemical feedstock (the fossil resource to build the polymer chain). The solid part of each bar represents the gross fossil energy use for the fuels and 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-

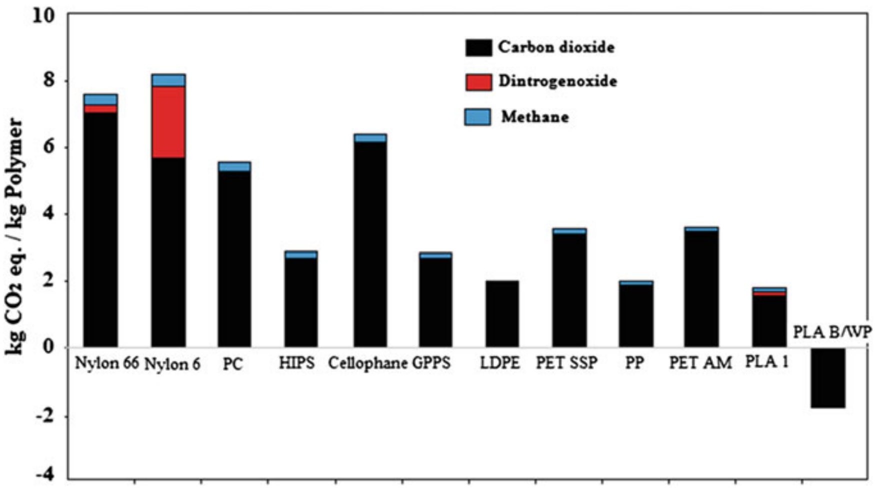


Fig. 13 Contributions to global climate change for some petrochemical polymers and PLA [38]

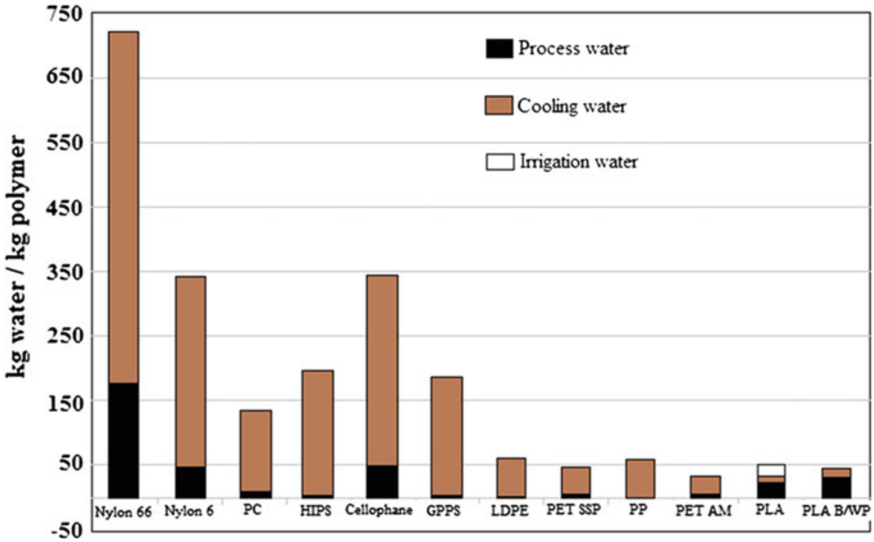


Fig. 14 Gross water use by petrochemical polymers and the two PLA cases [38]

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

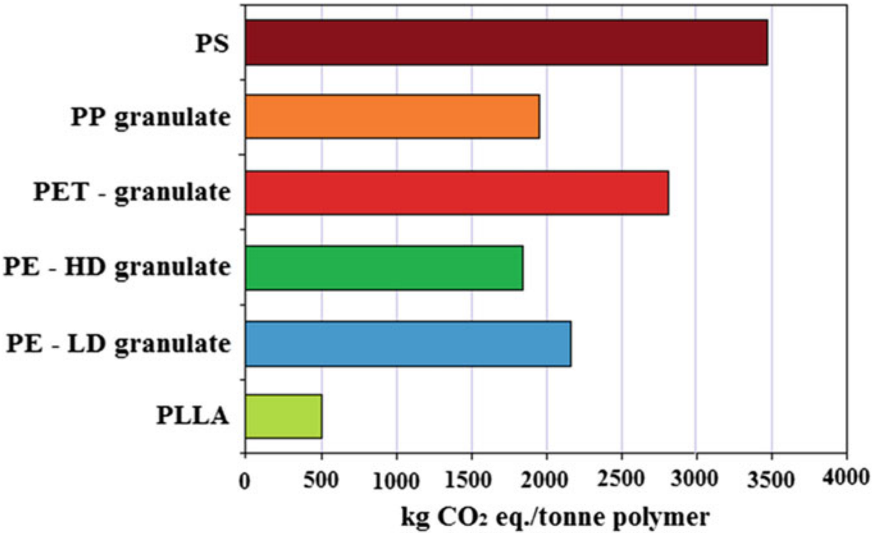


Fig. 15 GWP involved with the production of PLLA and other polymers

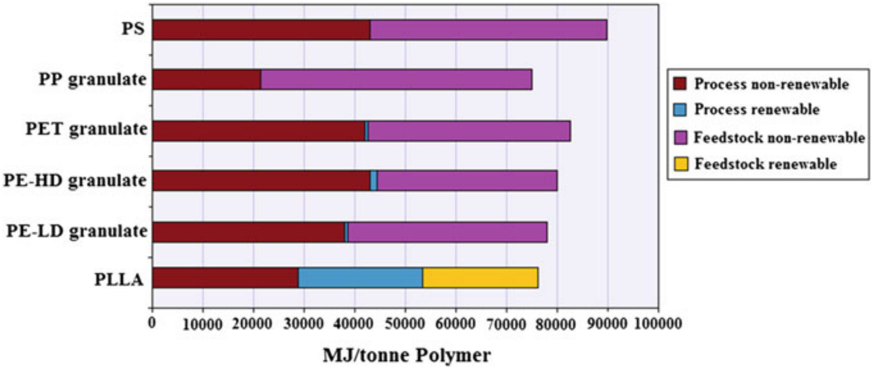


Fig. 16 Primary energy demand involved in the production of PLLA and other polymers

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.

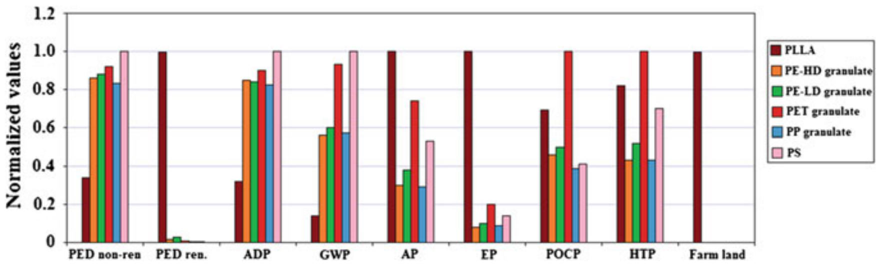


Fig. 17 Comparison of the most relevant ecological factors involved in the production of PLLA and fossil-based derived polymers

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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Textiles and Apparel Development Using Recycled and Reclaimed Fibers

Thilak Vadicherla and D. Saravanan

Abstract Sustainability is the latest buzzword across the globe that includes three aspects, namely the environment, economics, and society. With the emergence, acceptance, and obsolescence of fast fashion, textile wastes are growing to unprecedented levels at phenomenal rates. Textile wastes can be the raw materials for the developments of new value-added products through a proper recycling methodology. Textile waste management systems are currently undergoing a crucial phase, which aims to produce the value-added products through various recycling concepts and methods. Applications of preconsumer textile waste, postconsumer textile waste, and postindustrial textile wastes for the manufacture of home furnishings, branded apparel and accessories, concrete and composites, and other specialized products such as cleanroom garments, heating elements, and mountaineering equipment are discussed in the present chapter.

Keywords Accessories · Branded apparel · Composites · Home furnishings · Recycled/reclaimed fibers · Recycled yarns

1 Introduction

Sustainability, the catchphrase, looks very simple, but it is difficult to define, understand, and adopt in industry practices. An able definition was first given by Brundtland (formerly known as the World Commission on Environment and

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Textile Science and Clothing Technology, DOI: 10.1007/978-981-287-065-0_5,

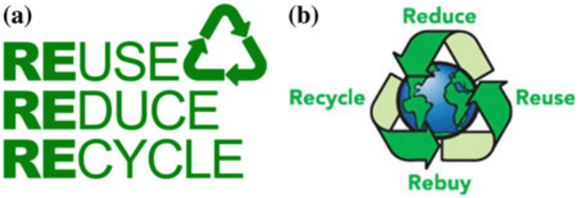


Fig. 1 **a** Concept of 3R and **b** 4R for sustainability

Development), in its report for the term *sustainable development* as "the development that meets the needs of the present without compromising the ability of future generations to meet their own needs" [1]. Adequate use of natural resources is vital for the sustainability of human beings on the earth, the earth as the whole, and the rates of natural resource generation and consumption should also match sustainability. The United Nations Environment Programme (UNEP), in its 2011 annual report predicted that the rate of consumption would become three times higher by the year 2050 with the present rate of consumption, taken into account, which puts an enormous amounts of stress on the already depleting scarce natural resources. One of the solutions to this ever-increasing problem would be the sustainable use of materials with the focus being shifted towards circular material flow (reuse, recycle) rather than conventional linear flow that relies on extraction, use, and disposal in landfills [2]. The need of the hour is to shift mankind's entire focus on either the 3R or 4R concept to adopt sustainability. The popular 3R concept comprises reuse, reduce, and recycle for the benefit of the environment, whereas the additional "rebuy" concept gives it another dimension and is aptly known as the 4R concept (Fig. 1a source: http://silversretro.blogspot.in/2011/01/reduse-reuse-recycle-and-repair-for-our.html and Fig. 1b source: http://sccomm.uga.edu/newsletters/fall06/4.htm respectively). It emphasizes the importance of rebuying products manufactured from recycled or reclaimed materials.

The typical sequences of processes adopted in the development of textiles and apparel using recycled or reclaimed fibers or a roadmap, may be adopted from Table 1. All the steps involved in the roadmap are elaborated upon at the appropriate places in this chapter.

2 Wastes, Methods of Recycling and Labeling

Recycling, a well-known and widely used terminology, necessarily consists of both downcycling and upcycling. Downcycling and upcycling aim to prevent wasting potentially useful materials, reducing consumption of raw materials, energy usage, and reducing air and water pollution. Downcycling is the process of converting waste materials or scrap products into new materials or products of lesser quality and reduced functionality. Examples of downcycling may include making a rug from clothing wastes and producing lower-grade plastic from

Table 1 Sustainability route through recycling and reclamation of textile wastes

Type of waste	Type of material(s)	Preprocessing steps	Processing	Possible sequence	Final or intermediate products	Demonstration of sustainability
Preconsumer/ Postindustrial/ Postconsumer	Natural fibers/ Regenerated fibers/ Synthetic fibers	Collect Sort label	Downcycling/ Upcycling	Mechanical	Recycled fibers/Reclaimed yarns and fabrics/Accessories/Garments and make-up	Labeling of products
				Chemical	Monomer /Oligomer /Polymer	

Table 2 Approaches for recycling

Approaches	Raw material for recycling
Primary approach	Industrial scraps
Secondary approach	Mechanical processing of postconsumer products
Tertiary approach	Pyrolysis/hydrolysis of polymeric wastes to get monomers or fuels
Quaternary approach	Burning fibrous solid wastes and utilizing the heat generated

recycling. Upcycling, the term introduced by Reiner Pilz of Pilz GmbH in 1994, is the process of converting waste materials into new materials or products of better quality, for better environmental values. Upcycling has seen an increase in use due to its current marketability and the lowered cost of reused materials. Popular examples of upcycling include making a rug from fabric scraps and producing a new skirt from old denims.

Recycling technologies are divided into primary, secondary, tertiary, and quaternary approaches based on the raw materials used and the products produced at the end of the process (Table 2). All four approaches also exist for fiber and fabric recycling [3, 4]. The US Environmental Protection Agency (USEPA) estimates that textile wastes occupy nearly 5 % of all landfill spaces and the textile recycling industry recycles only approximately 15 % of postconsumer textile wastes (PtCTW) each year, leaving a huge 85 % waste in the landfills. It could be attributed to high (40 %) rates of postconsumer textile waste generation and low (2 %) diversion rates [5]. Many organizations including the Council for Textile Recycling (CTR) are involved in creating awareness about keeping the postconsumer textile wastes out of the solid waste streams with a goal of achieving zero textile waste going to landfills by the year 2037 [6]. Textiles and apparel, being the major chunk of materials in landfills, reusing and recycling postconsumer textiles and apparel are gaining international attention.

Textile waste materials are broadly classified into three categories [7], including (i) preconsumer textile wastes (PrCTW), (ii) postindustrial textile wastes (PITW), and (iii) postconsumer textile wastes (PtCTW).

Preconsumer textile wastes are those wastes that never make it to consumers and which come directly from the original manufacturers. Following are the types of wastes that come under this preconsumer textile waste category and the list is not exhaustive.

- Ginning wastes
- Opening wastes
- Carding wastes
- Comber noils
- Combed waste yarns
- Roving wastes
- Ring-spinning waste fibers
- Ring-spun waste yarns
- Open-end spinning waste fibers

- Open-end spinning yarn wastes
- Knitting waste yarns
- Weaving waste yarns
- Fabric cutting wastes
- Fabric wet-processing wastes
- Apparel manufacturing wastes

Postindustrial textile wastes (PITW) are generated during the manufacturing process of upstream products. These are mainly from the virgin fiber producers, tire cord manufacturers, polymerization plants, and other plastic products.

Postconsumer textile wastes (PtCTW) are the wastes that come from the consumer and these are generally the clothes that are ready for disposal or landfill. They are recovered from the consumer supply chain. Favorite examples of the PtCTW include recycling of the accessories, beverage bottles to make recycled polyester.

Preferences for recycling of wastes appear to be predominant in thermoplastic polymer-based fibers due to the ease of processability and the ability to take on different forms and shapes after recycling. Nevertheless, natural fibers such as cotton, wool, and silk are also finding their ways into the recycling stream in terms of both downcycling and upcycling. The majority of the literature reported in the recycling of textile wastes includes polyester [8–33] followed by cotton, flax, linen [15, 30, 34–40], polypropylene [14, 31, 41], polyethylene [25, 36, 37], nylon [29, 42], p-aramid [43, 44], carbon [41, 45], silk [46, 47], polybutylene terephthalate [48], bamboo [28], and kenaf [15]. The recovered fibers, then, find their way to friction spinning [8, 9], rotor spinning [10], or comingling [41] methods with various functional finishes such as flame retardancy and UV protection [28]. Conversion of pre-/postconsumer textile wastes into final products consists of the following stages.

- Collection and sorting
- Fiber extraction
- Yarn preparation
- Conversion into fabrics and composites
- Finishing

Recycled fibers, yarns, and fabrics made of different textiles and polymeric bottle wastes possess physical properties [11–15, 33–37, 41, 49–53] similar to that of virgin fiber-based products. Many times, recycled fibers are supplemented with the addition of virgin polyester fibers, organic cotton, flax, and elastomeric fibers in order to achieve enhanced properties, aesthetics, and functional values.

Many voluntary and nonprofit organizations make attempts to conserve natural resources through various campaigns and create awareness of both downcycling and upcycling processes. Consumers are encouraged to use recycled products by creating esteem values (e.g., vintage look) for the products and providing labeling systems with different motives. With a view to conserve paper- and wood-based materials from postconsumer wastes, globally, a labeling system (Fig. 2a, source:

Fig. 2 Labels for recycled products **a** Forest stewardship council, **b** Global recycle standard, and **c** Bluesign

www.fsc.org) has been introduced by the Forest Stewardship Council (FSC) an international nongovernmental organization dedicated to address various deforestation issues. The FSC supports both recycled and reclaimed substances; however, such labels are issued only to products that contain 100 % recycled materials.

The Textile Exchange (earlier known as the Organic Exchange) of Texas is another nonprofit organization established in the year 2002 with a commitment to expand textile sustainability in the textile value chain across the world. It has introduced the concept of Global Recycle Standards (GRS; Fig. 2b, source: https://oecotextiles.wordpress.com) modified recently in 2012, includes recycling of pre- and postconsumer wastes and does not include preindustrial wastes inasmuch as many times such wastes are reintroduced into the main production stream and do not amount to recycling, instead diverting into the waste streams (e.g., wastes obtained in the drawing, roving, and spinning are reintroduced in the blowroom or reusing the polymeric wastes back into the same process). GRS provides a three-tier (level) system based on the total content of recycled material in the final products. The gold standard offered by the GRS is meant for products containing 95–100 % recycled materials, whereas silver and bronze standards include final products with recycled content of 70–95 % and a minimum of 30 %, respectively.

Bluesign is another labeling system (Fig. 2c, source: http://business-ethics.com/2012/11/11/what-is-the-bluesign-standard-for-textiles) promoted by the Bluesign Technologies AG, Switzerland-based organization which also audits the manufacturing processes, energy inputs, and air emissions from various processes. Each component used in the process is examined based on ecotoxicological issues and the possibilities to reduce consumption and suggest the alternatives. Textile waste-processing units are expected to adopt verifiable procedures, processes for such labeling standards; Bluesign labels are issued to socially conscious versions of jackets, pants, shirts, sweaters, and accessories such as hats and gloves.

All these initiatives are expected to promote environmentally appropriate, socially beneficial, and economically viable management systems of various waste streams and waste materials from preconsumer wastes, postindustrial wastes, and postconsumer wastes, in general. Many more players work on providing the labeling to recycled and reclaimed products. Textile waste recycling and reclaiming industries, which process significant amounts of waste generated globally, are expected to benefit from these standards on many fronts.

2.1 Natural Fibers

Preconsumer or postconsumer cotton wastes are again converted into yarns and subsequently to fabric forms. Fabric-breaking machines along with yarn-opening attachments help in opening up the fibers and the opened fibers are spun into coarser yarns by ring, rotor, and friction spinning processes.

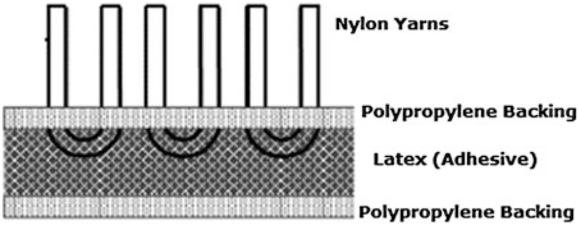
2.2 Synthetic Fibers and Polymers

The Society of the Plastics Industry (SPI) established a classification system [54] in the year 1988 to allow consumers and recyclers to identify and differentiate various types of plastics, on which the manufacturers print an SPI code, or number, on each plastic product, usually molded on the bottom portion.

1. Polyethylene Terephthalate (PET)
2. High-Density Polyethylene (HDPE)
3. Polyvinyl Chloride (PVC)
4. Low-Density Polyethylene (LDPE)
5. Polypropylene (PP)
6. Polystyrene(PS)
7. Miscellaneous plastics: Polycarbonate and Polylactides

Recycling polyester from the PET bottles is achieved either by mechanical recycling or chemical recycling processes. However, collection and sorting of the polyethylene terephthalate (PET) bottles are the initial steps for both processes. PET bottles are initially sorted and separated from other materials including glass, cartons, metals, PVC, HDPE, LDPE, polypropylene, drink cartons, and so on. A second sorting is done as per the color fractions such as transparent or uncolored polyester, blue and green colored, and the remainder into mixed colors fractions. In many places, crushed bottles are sold in bales of various sizes after commercialsorting .

Fig. 3 Carpet structure



2.3 Mechanical Recycling

Mechanical recycling is basically a melt extrusion process that consists of contamination removal and the melting of polymer flakes. Sorted polyester wastes are ground to flakes, and washed with detergent or solvents to remove the contaminants. Flakes are dried thoroughly to prevent deterioration of the products through hydrolytic degradation. These flakes are melted, extruded, and preferably cross-linked to improve the mechanical properties. PET flakes are used as the raw material for a wide range of products that would otherwise be made of virgin polyester fibers, such as yarns and other products. Examples include polyester fibers (for the production of clothing, pillow infills, carpets, etc.), polyester sheets, strapping, or back into PET bottles and containers.

Nylon is another fiber to be recycled and reclaimed to a larger extent, similar to that of polyethylene terephthalate from blankets and carpets. Polypropylene, nylon, latex, and PET are some of the fibers and polymers widely used in carpets (Fig. 3, source: Wang Y., *Recycling in Textiles, Woodhead Publishing*, Cambridge, UK, 2006), which are also widely recycled among synthetic fibers. In general, face yarns are made of either texturized nylon 6 or nylon 6,6, primary backing and secondary backing of polypropylene, sandwiched with an adhesive material. On the basis of weight, face yarn, backing, and adhesive accounts for 50, 20, and 30 %, respectively.

2.4 Chemical Recycling

Chemical recycling aims to reduce the polymers into various levels such as oligomers or monomers, which in turn can find different applications including polymerization to get the same polymers and fibers again [55]. However, this process normally requires high temperatures and pressures, and takes a long time for the treatment. Depolymerization of polyethylene terephthalate includes three separate processes, namely hydrolysis, methanolysis, and glycolysis. In hydrolysis, polyethylene terephthalate is depolymerized to terephthalic acid (TPA) and ethylene glycol (EG) in an acid or alkaline or neutral environment. Methanol depolymerizes polyethylene terephthalate to dimethyl terephthalate (DMT) and ethylene glycol (EG). Ethylene glycol partially depolymerizes PET into oligomers. This process produces *bis* (hydroxyethyl) terephthalate, which in turn can be polymerized into PET again.

Nylon 6 is often depolymerized using a closed-loop recycling process using chemical distillation (BASF) or selective pyrolysis and continuous hydrolysis (Evergreen Nylon Recycling LLC). Solvent extraction of nylon is also carried out using supercritical fluids, aliphatic alcohols, alkyl phenol, hydrochloric acid, and formic acid for separation of impurities and polymers.

2.5 Mechanical Separation

Size reduction and the separation process involve a two-step process developed by DuPont [56, 57] that consists, first, of a dry process where a series of size reduction and separation steps provides a dry mix of 50–70 % nylon, 15–25 % polypropylene, and 15–20 % latex and fillers. Addition of water to the dry mix in the subsequent step facilitates washing and separation of the shredded fibers due to the density differences between fillers and fibers present in carpets such as nylon and polypropylene. Two separate streams of pure nylon and polypropylene are obtained and usually recycled nylon is compounded with virgin nylon at a ratio of 1:3 and recommended for making automotive parts.

Recycling of nylon from postconsumer carpets (PtCTW) is achieved by either a mechanical process sequence, solvent extraction processes, or depolymerization methods [42]. Collection, sorting, and size reduction are the initial steps for these processes. Once the postconsumer carpet wastes are collected, they need to be sorted either manually, with an automatic melting point indicator, or through infrared spectroscopy identification. Shredding and grinding processes are employed for size reduction of the wastes.

3 Recycled Yarns

Yarn production from recycled materials paves the way for the production of fabrics and other value-added products. Various reports available on the production of recycled yarns suggest that yarns can be produced using friction spinning to produce a medium (40 s) count (linear density) yarn from the PET recycled fibers [8, 9]. Rotor spinning is another widely used spinning technique for the production of recycled yarns and, optimum opening roller speed for the successful spinning of polyester/waste blended rotor yarns has been recommended with other process parameters [10]. Comparison of yarns produced from recycled fibers and virgin fibers [11] shows that tenacity and elongation values of yarns obtained from recycled fibers differ marginally, however, such processes appear to be economically advantageous in the long run [12]. Nevertheless, spinning of recycled and reclaimed fibers using ring spinning has also been a favorite option for many manufacturers.

4 Fabrics from Recycled Yarns

Recycled fibers and yarns are predominantly used in manufacturing home furnishings [44, 46, 47], reinforced concrete, and polymeric composites [15, 35–37, 49–52, 58–60], towels [19, 39], shoddys, carpets, floor coverings [20, 22, 53], wipes [44, 61], accessories [17, 25, 48], nonwovens [18, 53, 61], and acoustic insulators [38, 62].

Commercially, many manufacturers offer a wide range of woven/knitted/nonwoven fabrics manufactured from recycled materials (details are discussed below), however, very little information have been reported in the literature regarding their aesthetic, utility, and durability and comfort properties.

A study carried out to examine the performance and durability of woven fabrics manufactured from recycled polyester fibers [13], extruded from PET bottle wastes, reveals that with an increase in the recycled polyester fiber content, bending rigidity and shear stiffness values increase. However, durability tests reveal that the bending rigidity and shear stiffness values decrease on repeated washing and fatigue measures such as higher hysteresis and lower resilience values are not clear

Another study of recycled T-shirt cotton fabrics reveals the effect of home laundering on the physical properties in comparison with virgin cotton fabrics of similar construction [34]. T-shirt fabrics produced with recycled cotton fibers, compared to the T-shirt fabric produced from virgin cotton fibers, show a tendency to shrink in the course direction possess decreased air permeability, and a small change in bending rigidity in the wale direction. Chlorine-based bleaches are successfully applied in bleaching of recycled cotton fabrics [63] to eliminate the dirt and impurities associated with the fabrics produced from yarns without losing the properties significantly.

Conductive textiles are usually manufactured with the use of metal strands while weaving the textile fabrics or coating the fabrics with conducting polymers. Conductive fabrics have been developed with recycled nonwoven polypropylene and analyzed for their electrical properties [14]. Complex core-spun yarns have been used in the development of conductive fabrics with core yarns spun from the recycled pieces of polypropylene nonwoven selvedges (PITW) and the wrap yarns with 80-μm stainless steel wires. In order to reinforce the core-spun yarn, 80-μm stainless steel wires and 80-μm copper wires, parallel to the core yarns have been recommended with wrap numbers of 0.5, 1.5, 2.5, 3.5, and 4.5 turns/cm.

Fabrics are woven with PVC-coated polyethylene terephthalate (PET) filaments as the warp yarns and complex ply yarns as the weft yarns are evaluated for surface resistivity and electromagnetic shielding effectiveness and the fabrics with varied lamination angles provide good electromagnetic shielding capabilities [14].

5 Concretes and Composites

Recycled fiber-reinforced composites using cotton, flax [35–37], kenaf [15], carbon [41], PET [16], and cement concretes using natural and HDPE [35–37, 41, 50, 58–60] have been developed in the past. Concrete structures, widely used for construction purposes, are relatively brittle with their tensile strength values typically about 1/10 of compressive strength values and regular concrete structures are generally reinforced with steel rods or bars of different dimensions and grades. These days, chopped randomly distributed fibers are also being used to reinforce concrete, which in turn results in increased absorption capacity, toughness, and tensile and flexural strength of the concrete structures. Concrete reinforcements with recycled fibers have been studied extensively in the past with the fiber elements reclaimed from tire cords, carpet industry wastes, feather fibers, steel shavings, wood fibers, and high-density polyethylene [35–37, 41, 50, 58–60]. From the available literature, a direct comparison of properties is not possible because of the differences in concrete configurations and manufacturing processes. Nevertheless, a general trend is observed that the recovered fibers could provide similar reinforcement as virgin materials, but a higher dosage rate may be required to match the performance.

Composites made out of flax, cotton, and recycled polyethylene [35, 36] exhibit higher fabric strength with the increase of blend percentage of flax fibers obviously due to their inherent properties, although the elongation values decrease. Apparently, the effects of moisture on composites made from recycled composites have been analyzed [49–51]. Recycled p-aramid fibers [43] have also been analyzed for their thermal and mechanical behaviors. Thermal and water sorption properties of polyethylene and linen yarn production waste composites polyethylene/linen waste combinations with filler content of 10–50 wt%, without and with modifiers have been investigated extensively and the effects of diphenylmethane diisocyanate are found to be well correlated [37].

Kenaf fibers combined with cotton combing wastes and sheared polyester wastes with polyester resin as matrix exhibit comparable results to those of glass fiber-reinforced composites. The flexural properties of kenaf-fiber–reinforced composites are on par with glass-fiber–reinforced composites. Results also indicate that, with an improvement of fiber lay-up, the properties of kenaf combined with cotton comber wastes are on par with glass composites and flexural rigidity may even be on the higher side than glass-fiber–reinforced composites.

Thin composite boards [15] have been manufactured with the noils obtained from the cotton combing process, blowroom wastes, and polyester resin at room temperature utilizing a compression method. Tests on tensile and flexure properties of these composites reveal that composites made from cotton wastes are significantly much stronger than polyester matrix, and these composites show the potential to replace wood and fiber-board products as the thin boards.

Recently, readymade garment wastes (PITW) reinforced polymer composites [52] have been examined for their mechanical properties, and show positive results. Thermoplastic composites manufactured from commingled carbon fiber/polypropylene yarns with polypropylene matrix exhibit good tensile and flexural strength values, 160 and 154 MPa, respectively, for composite specimens containing 28 % commingled carbon fiber by volume (fiber volume fraction) and such composites are recommended for nonstructural applications [41].

Imperial Chemical Industries (ICI, United Kingdom) with its two distinct product lines for recycling textile waste materials [16], *Structure-Lite*, and *EcoScape*, is marketing unique products to a wide variety of industries. *Structure-Lite* composite panels are made of recycled polyester, recommended to the transportation industry as cargo containers, truck body containers, and highway sound barrier panels; such panels offer unmatched durability and strength compared to similar lightweight panels made from other materials. The advantage of the thermoplastic skin in *Structure-Lite* composites is that they can be formed into different shapes, making them ideal for the transportation and marine industries. *EcoScape*-based houses, designed with the adaptation of *Structure-Lite* panels offer easy and fast assembling combined with high strength and durability, ideal for natural disaster situations and relief camps.

6 Home Furnishings

Home furnishings have been the primary focus for using recycled fibers, yarns, and fabrics for many of the manufacturers and polyester [19–21, 23, 24, 39], cotton [28, 38, 39, 44, 61], silk [46, 47], aramid [53], and polypropylene [62] fibers are widely used for various products. Preconsumer textile wastes and postconsumer textile wastes are used equally in the production of home furnishings and post-industrial textile wastes are also gradually being introduced in such products.

EcoSure® offered by the Poole Company (South Carolina) consists of recycled fibers that are manufactured using 100 % postconsumer recycled materials, with a linear density range of 1.2–500 denier [18], suitable for outdoor furniture, roof vents, industrial scrub pads, and also apparel. The proprietary process makes the bottle-grade polymers more elastic compared to virgin-fiber polymers. Wipes produced using *EcoSure* are as good as those of virgin fibers and moreover they also provide softer and gentler products. The process flow includes collection of PET bottles, sorting, washing, grinding to flake, sanitization, fiber extrusion, and finally wipe manufacturing. These fibers can also be used in the manufacturing of nonwoven fabrics, through either spun lace or thermal or adhesive bonding methods, as well as needle-punching processes. Recycled polyethylene terephthalate fibers with a linear density of 1.2 denier are recommended for hygiene-grade technical nonwovens and 500 denier fibers are used for the production of industrial scrub pads.

Disposable and hygienic pillows have been developed [23] with the filling made from 100 % recycled, expandable polyester and covered with nonallergenic nonwoven fabrics, which are further recyclable.

Marks and Spencer, the leading British multinational retailer headquartered in London, also supplies pillows with supremely washable, soft touch, medium support characteristics [24] with nonallergenic fillings made from recycled plastic bottles that makes the products machine washable at 50 °C.

Finished yoga towels from recycled materials [19] are manufactured by Guru Athletics (Ontario) with 80 % polyester derived from recycled plastics pop bottles (PtCW) and comprised of 20 % natural cotton fibers.

Shaw Floors (Georgia), an exclusive manufacturer of carpets and floor coverings, started a dedicated manufacturing line of carpets in the year 2005 under the trade name *ClearTouch Carpet* [20], which features *ClearTouch*® BCF polyethylene terephthalate filament with significant recycled components (PtCW). *ClearTouch*, a continuous filament, offers the inherent attributes of polyester as well as exceptional performance characteristics, such as excellent appearance retention and long-term wear. These yarns are also produced with exceptional softness and such products are marketed under *Texturegard*, a concept incorporated to introduce the texture retention warranty. The patented process of Shaw Floors, *R2x*, offers twin resistance against stains and soils for protection against spills and tracked-in dirt.

Pottery Barn, a home textiles chain based in San Francisco, offers unique *senna antique kilim rugs* used for decorative purposes [21], consisting of recycled polyester yarns, woven on a handloom. Such rugs offer a soft and smooth texture with durability.

Regenerated Cotton Wipes from Rockline Industries (Wisconsin) won the Visionary Award for the most innovative use of nonwovens in consumer products for the year 2010 [61]. The USP of recycled cotton fibers includes variability in length, and use of dark colored and white fibers separately, in addition to other sustainable parameters (PITW). Composting of such recycled wastes degrades more than 90 % in 28 days.

Strateline Industries LLC (Arkansas) makes wet wipes from fibers recycled [44] from fabric cuttings supplied by T-shirt factories located in various parts of China (PITW).

Cotton Incorporated has partnered with Bonded Logic Inc. of Arizona to collect discarded blue cotton jeans (PtCTW) for reprocessing into insulation materials that are donated for use in houses built by Habitat for Humanity [38]. Similar concepts are also used by Blue Point Living (Florida) which offers recycled towels [39] using the raw materials obtained from preconsumer recycled cotton to the extent of 25 %. The recycled fiber yarns are manufactured using 65 % virgin cotton fibers, 10 % polyethylene terephthalate, and the remaining content from recycled cotton fibers.

MebRure Studio (Turkey) offers a wide range of eco-furniture [46] manufactured using white oak and recycled silk coverings filled with spongy stuffs. Silk and spongy combinations are expected to provide a unique and luxurious experience to consumers.

Vaibhav Resham Udyog (India) uses extensively recycled silk yarns [47] that are made from leftovers and scraps of contemporarily produced Indian saris, an ethnic wear of the country. Branded yarns from the silk wastes, Himalaya or Himalayan yarn, Nepalese Yarn, Rungy Chungy yarn, and Tibetan yarns are produced using recycled fibers, and used for value-added ladies garments, home furnishings, and silk ribbons.

Leigh Fibers of South Carolina has established manufacturing facilities to reprocess postindustrial fabric wastes of both natural and manmade fibers into products suitable for use in a wide range of nonwovens and other under-the-surface applications as well as for remelting and subsequent spinning into different linear densities [53]. *SafeLeigh* flame-retardant (FR) aramid fibers recycled from postindustrial clippings provides the advantage of inherent FR properties for needle-punched and air-laid nonwoven furniture components, mattresses, and automotive parts. Blends are also produced using virgin and reclaimed waste materials, and synthetic and natural fibers. Various grades of fibers produced include grades for air-lay where products are designed to be run on air-laid forming machines, grades for garneting, and, grades for blowing, where short fiber blends are designed for use in blowing applications. In addition to needle-punching, *SafeLeigh* products are amenable to processes including thermal bond and pad-making. It is also claimed that cotton, rayon, acetate, polypropylene, acrylic, and other textile wastes are used in many under-the-surface applications as well as wet wipes.

Newlife™, continuous polyester yarns from 100 % recycled postconsumption PET bottles mainly through mechanical processing, is seen as the source of the prestigious red carpets of the world, endorsed by divas and celebrities, on account of the collaboration with CLASS, Creativity, Lifestyle and Sustainable Synergy [22]. Manufacturers of *Newlife* claim the possibilities of using the yarns for different applications in every subset of technical textiles, including awnings, outdoor clothing, sportswear and technical outfitting, underwear, work wear, medical and protective clothing, home furnishings, and interior and outdoor design fabrics.

Research work carried out on the developments of acoustic underlay products from recycled carpet wastes [62] have shown positive results and reinforce the assurance for the commercially viable products. Laboratory trials performed on the recycled underplays, manufactured with recycled carpet wastes and styrene–butadiene binders are compared with commercially available products, produced with standard granulating PVC-back, nylon/polypropylene piles and binding. Recycled underlay performs well in the ISO 140–8 test for impact sound insulation of floor coverings as well as BS 5808 specifications. Combinations with appropriate backing scrims in the recycled underlays ensure the impact performance of such materials and facilitate value-added products.

7 Branded Accessories and Apparel

Accessories such as fasteners (snap fasteners, buckles, hooks, zippers), components of shoes (uppers, mid- and insoles), and branded garments are produced using recycled fibers and fabrics. Many manufacturers began their efforts as early

Table 3 Brands/collections/companies producing apparel and accessories using fibers and polymer wastes

Fiber	Product(s)	Type of wastes	Brand/ Collection/ Company	References
Poly (ethylene terephthalate)	Zippers, sliders, chains	Postconsumer polyester waste	Natulon/YKK	[34]
Poly (butylene terephthalate)	Buckles and adjusters	Postconsumer polyester waste	Natulon /YKK	[34]
Corn material	Zippers	Preconsumer waste	ReEarth /ICI	[35]
Polyester	Fashion garments	Postconsumer textile waste	*Conscious Collection*/ H&M	[52]
Poly (ethylene terephthalate)	Khaki trousers	Postconsumer recycled plastics	*Dockers / Levi's*	[53]
Poly (ethylene terephthalate)	Sports jerseys and shoe uppers	Postconsumer recycled plastics	Nike	[54]
Wood fibers	Mid-soles of shoes	Recycled cardboards	*Adidas*	[55]
Poly (ethylene terephthalate)	Sportswear	Postconsumer polyester waste	*Adidas*	[55]
Poly (ethylene terephthalate) and bamboo fibers	Low-cut socks	Postconsumer polyester and bamboo wastes	Asics	[61]
Nylon	Beach wear	Postconsumer nylon waste	Beachwear Collection/ Esprit	[29]
All fibers	Coats and jackets	Discarded garments	Shwop coat/ M&S	[58]
Cotton and poly (ethylene terephthalate)	Sportswear	Postconsumer textile wastes	EcoSmart/ Hanes	[60]
Poly (ethylene terephthalate)	Track jacket	Postconsumer textile wastes	*InCycle/Puma*	[62]
Plastic wastes	Inner soles of shoes	Biodegradable plastics	*Sustainable Soles/Gucci*	[63]
Leather	Hook set collection	Leather wastes	*Earthkeepers*/ VFCorp	[65]

as the early 1990s and made a significant impact among consumers across the globe. Esprit was known for its organic collection in 1992, making it one of the very few sustainable apparel industries at a time when the sustainability concept was in its nascent stages [29]. Table 3 shows the brands of various apparel and accessories manufactured under different brand names with the respective sources of waste materials.

YKK of Japan offers zippers made from recycled polyethyelene terephthalate under the brand name *Natulon* [17]. First of its variety in this line, it consists of eco-friendly coil zippers whose open metal part is replaced by recycled PET and the second variety includes both chain and slider of zippers made from recycled materials, that is, postconsumer recycled polyester. Also, these products have no metal components, which enables these zippers to be easily broken down and easily recycled perpetually. *Natulon* adjusters and *Natulon* buckles are recycled poly (butylene terephthalate) products produced by YKK in this range. Velcro, a hook and loop structure of *Natulon*, is made of recycled polyester (58 %). *Sofix* is another innovative product that comes under the category of snaps and buttons, which has a plastic component of the snaps injected onto knitted PET tapes, suitable for joining two ends.

ReEarth zippers [48] of ICI comprise corn and other plant materials that helps to introduce the concept of biodegradability in an appropriate composting environment.

Patagonia was one of the first apparel manufacturing companies to initiate sustainable efforts, during early 1990s [64]. Patagonia is the first outdoor clothing manufacturer that creates fleece made from postconsumer recycled plastic soda bottles and Patagonia's other sustainable campaigns such as "*Buy Less*" and "*Don't Buy This Jacket*" have colossal positive impacts on customers' awareness of sustainability.

H&M is one of the few brands that started green fashion in the middle 1990s by launching the Conscious Collection, using organic cotton fibers [25]. It's second "Conscious" collections include partywear made from recycled polyester (PtCTW) and organic cotton. Other garments of the collections are made up of organic cotton, organic linen, and Tencel. This collection has clothing for women, men, and children. Men's *Brick Lane Bikes* is another sustainable collection from H&M, in which garments are manufactured from organic cotton, recycled polyester, and recycled wool. Other sustainable collections include the Conscious Glamour Collection that features jewel-toned frocks and punchy neon gowns. Standard plastic consumer bags of H&M are made up of 50 % postconsumer and 50 % preconsumer recycled polyethylene.

Levi's lifecycle assessment of 501 jeans and Dockers, conducted in the year 2007 paved the sustainability roadmap for the coming years [40]. The surprising results indicate that nearly 50 % of water is consumed in cotton harvesting, another 45 % of water is used by consumers during washing, and nearly 60 % of the energy is used in making and taking care of a pair of jeans. Levi's *Waste-Less*$^{\text{TM}}$ *Jeans* consist of at least 29 % postconsumer recycled plastics made from eight plastic bottles. Levi's *Waterless*$^{\text{TM}}$ denims aim at reduction of water consumption during manufacturing and are produced by using ceramic stones, rubber balls, and changing the filtration system in the washing machines to enhance mass transfer actions, which facilitates the reduced water consumption. A distressed look is achieved with just four liters of water, whereas normal styles require up to 45 liters of water per pair of denim jeans.

Nike, with its sports jerseys for the 2010 FIFA World Cup that were made from recycled plastic bottles, has created awareness of sustainability across the globe in a positive manner [26] and *Flyknit*, an innovative manufacturing process that reduces waste in knitted fabrics is used in the upper parts (shoe uppers) of shoes.

Other sustainable efforts from Nike include Nike Materials Sustainability Index (Nike MSI), a tool for designers to create products with lower environmental impacts, exploring new materials and manufacturing processes through their Sustainable Business & Innovation Lab, a leaner and greener supply chain.

Adidas is well known for its association with the London Olympics 2012 in making the world's first truly sustainable Olympics initiatives. Fluid Trainer, the most sustainable shoes ever as claimed [27] by Adidas, is designed in such a way that it reduces waste in shoe upper designs. Shoe uppers of Fluid Trainer consist of nearly 50 % recycled contents in the upper, and 20 and 10 % regrinds into the sock liner and soles, respectively. *For Motion Soles* introduced by Adidas, use 50 % less material in the production than that normally used in a typical sole of a sports shoe. *Green Silence Shoe* incorporates soy-based inks, biodegradable midsoles, and recycled materials. In addition, 100 % recycled cardboard sneakers have been introduced by Adidas for their spring/summer 2014 collection, which are subsequently recycled to produce stormtrooper helmets and injected plastic plates used in the football boots. Adidas jackets and shirts made from 100 % recycled materials were worn by London Games volunteers and 70 % of competitive wear worn on the field by athletes had significant sustainable content, with materials such as high-performance recycled polyester made from recycled water bottles. Adidas developed 65 sustainable performance fabrics exclusively for the London Olympics. Also, 100 % of Athlete Village Wear, Torch Relay, and London Games volunteer kits were made from recycled contents. Adidas jointly with Carvico and Aquafil, produces high-performance swimwear from 100 % recycled polyamides from postconsumer materials, suitable for swimsuits and trunks.

Hera Bamboo low-cut socks [28] is a sustainable invention by *Asics*, made up of a blend of recycled polyester fibers and bamboo fibers. *Asics* Men's ARD SS Run Shirt adds another feature, a finish with recycled coffee grounds that facilitates UV protection with a UPF of 50+.

Most of the garments manufactured by Espirit (Hong Kong) are from either 100 % organic cotton, or cotton in conversion or organic linen or Tencel or a blend of these fibers, from as early as 1992. Esprit was the one of the first labels to produce a beachwear line using recycled nylon under the Beachwear Collection 2012 in which a blend of 70 % recycled nylon and 30 % Lycra were used for their manufacture [29]. Subsequently, the Beachwear Collection 2013 saw a series of garments including eight tops and bottoms, made up of more than 82 % recycled nylon and 20 % elastomeric fibers. The environmentally friendly Esprit clothing range also includes garments made up of 100 % recycled polyester. Esprit's recycled collections are Global Recycle Standard (GRS) certified, for the garments that contain at least 30 % recycled contents.

Marks & Spencer unveiled its first *Shwop coat,* made from recycled fabrics collected through its Shwopping initiative [65], where customers can drop in unwanted items of clothing regardless of brands and values. It is said to have collected about 6 million items through this initiative, whose benefits are passed on to Oxfam, a nonprofit organization that helps to find solutions to mitigate poverty across the world.

EcoSmart by Hanes, one of the oldest branded clothing, is the well-known trademark for fibers made with recycled contents, both polyester suitable for socks, sweatshirts, sweatpants, fleece garments, and corrugated packing and cotton fibers [30]. *EcoSmart* men's black athletic socks contain at least 55 % recycled cotton fibers, and the white socks are produced with 15 % recycled yarn contents. Hanes sweatshirts and sweatpants are produced with at least 5 % *EcoSmart* polyester fibers.

Puma's *Bring Me Back* program has played a great role in the recycling process [31]. Puma's *InCycle* is a sustainable collection that includes shoes, apparel, accessories, and home insulation materials made up of either biodegradable polymers, or recycled polyester and organic cotton. It introduced a successful program, "100 % Cradle-to-Cradle," basic certified collection that has the facilities to collect lifestyle sneakers (biodegradable), legendary Puma Track Jacket (recyclable), shirts (biodegradable), and backpacks (recyclable) from the general public. The recyclable Puma track jacket is made up of 98 % recycled polyester and 2 % elastane. Puma's backpack is made up of polypropylene and new backpacks can be developed from the recycled Puma backpack. The upper part of Puma's biodegradable lifestyle sneaker, "Basket," is made up of a blend of organic cotton and linen and the sole comprises the biodegradable plastic *APINAT Bio*, which is biodegradable when disposed of correctly. Puma's Re-suede uses 100 % recycled materials and an outsole with rice-husk fillers in place of rubber components.

Gucci (Italy) has earned its reputation by developing sustainable eyewear [66] manufactured from liquid wood, a composition of biobased materials that represent an alternative to plastic-based materials. Now, it has come to the sustainability forefront, with its new *Sustainable Soles*, a line of footwear made with biodegradable plastics sourced from the composting process. Gucci has also introduced new FSC-certified 100 % recyclable packaging for Gucci brand eyewear.

Volcom boasts of organic denim made from 100 % organic cotton, ozone bleaching, and laser finishing to reduce environmental impacts caused by conventional chemicals and auxiliaries [67].

VF Corporation (North Carolina) has introduced the *Earthkeepers* Hook Set Collection, handcrafted collections that feature a minimal amount of materials, including organic cotton, natural latex rubber, and recycled aluminum and leather pieces [68]. *Timberland*® products also utilize recycled polyethylene terephthalate, *Smartwool* faux shearling coats and jackets made from merino wool and recycled PET, Polartec fabrics, and bionic canvas materials.

8 Technical Textiles

Many technical textiles such as indutech [69], sportech [32], agrotech [70], meditech [18], and clothtech [33] are produced using recycled fibers and fabrics. Also, it can be expected from the existing trend that use of various waste materials is expected to increase in the coming years due to the wide range of applications existing in technical textiles.

Cleanroom garments provide increased levels of protection against the entry of particulates into the cleanrooms and other controlled environmental conditions. Disposable cleanroom garments have the potential to reduce the possibility of toxic contamination to a greater extent. Cleanroom garments and accessories including gloves, hoods, boot covers, and hairnets were originally considered hard to recycle, a paradigm that has been redefined by *TerraCycle* (New Jersey) by developing an appropriate methodology [69] to convert these wastes into value-added raw materials to create useful, eco-friendly consumer products. Plastic Adirondack chairs and benches are some of the items manufactured using the recycled materials obtained from these sources.

A heating element material has been developed using recycled carbon fibers. Recycled carbon fiber nonwoven sheets in sandwich [45] form possess impressive electrical conductivity (around 2.8×10^3 S/m) and high durability to withstand up to 3,000 double folds under a durability test. These fabrics are ideally suited for usage in various heating garment applications as well as for food packaging and delivery systems.

DyerSport ECO is the trade name of double-sided brush fleece manufactured by Dyersburg Corporation with recycled fibers [33]. In 1992, the first postconsumer recycled ECO (Environmentally Correct Origins) fleece fabrics were made from recycled plastic soda bottles, Lite in 1996, and the fabrics for technical underwear and outerwear in the year 1998. *DyerSport ECO* Fleece, a joint venture of Dyersburg Fabrics, Patatgonia, and Wellman Inc. is produced entirely from recycled soda bottles and such fabrics are specifically designed for durability, warmth, high thermal insulation (Clo) ratings, low pill finishes, stretch, and other applications. The versatile fabrics offer a lush feel and moisture management, combined with strength, breathability, and shrinkage control.

Mountain Equipment Cooperative (Toronto) manufactures 53 % of branded apparel approved by *Bluesign* materials for sustainable textile production, which essentially means the compositions are at least 50 % organically grown cotton or recycled polyester fibers, or completely PVC-free products [32].

Wipes produced using the *EcoSure* are as good as those of virgin fibers and used in the manufacturing of nonwoven fabrics [18], through either spun lace or thermal or adhesive bonding methods, as well as needle-punching processes. As stated earlier, recycled polyethylene terephthalate fibers, with a linear density of 1.2 denier, are recommended for hygiene-grade technical nonwovens.

EarthGuard is the trademark of Earthguard, Inc. (Washington), the erosion-control product that includes recycled carpet fibers [70]. *EarthGuard* Fiber Matrix is a patented methodology that combines EarthGuard and also the fibers to form a matrix that provides extended erosion control protection in severe situations with easy deployment facilities. *EarthGuard* currently offers many varieties in this domain, including *EarthGuard Fusion*, *EarthGuard Edge*, *EarthGuard Organix*, and *EarthGuard Elixir*, ideal for agricultural applications in remote areas with limited water supply and smaller farms where hydromulching is cost prohibitive.

EarthGuard Fusion is a hydraulic growth medium and mulch (HGM^2) product that combines erosion control with the agricultural benefits of fertilizers and growth stimulants making it ideal for any revegetation application. *EarthGuard Organix* is a high-quality top soil replacement product classified as the hydraulic growth medium (HGM) that has the benefits of *Organix* by adding Terra Novo's line of fertilizer and growth stimulants. *EarthGuard Elixir* stimulates biological activity and biodiversity, providing necessary nutrients to maximize plant growth.

9 Future Prospects

The USEPA estimates that the textile recycling industry recycles approximately 15 % of all PtCTW, which essentially means the remaining 85 % of PtCTW has yet to find applications in recycling. An inclusive approach is very necessary to increase the usage of recycling content in developing new products. Designs of easy-to-recycle products, improved technology for the collection, sorting and processing of textile wastes, development of low-cost innovative products available on a commercial scale, and increased customer awareness are some of the vital points to improve the usage of recycled products. If governments can also provide regulations and implementation measures for the incentivized utilization of recycled contents in textile products, it will be a boon for the textile recycling industries. Consumers and customers with an increased focus on the use of recycled products can also definitely increase the recycling prospects of textile products. Further research into the development of garments from alternative natural fibers, development of durable and comfortable garments from 100 % recycled and reclaimed fibers, zero waste garments, seamless garments, and garments produced from a single machine will be interesting and challenging for the textile technologist and innovator.

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Environment-Friendly Textile Processing Using Plasma and UV Treatment

Kartick K. Samanta, Santanu Basak and S. K. Chattopadhyay

Abstract Wet chemical processing of textiles requires a large quantity of water as a processing medium, which is finally discharged as an effluent contaminated with residual dyes, pigments, and other hazardous chemicals. However, plasma and UV photons can be effectively used for nanoscale surface engineering of various textile substrates while avoiding the usage of water as a processing medium. Plasma- and UV-induced surface activation, oxidation, etching, increase in surface area/roughness, and polymerization of textile substrates have also been utilized for improvement in water and oil absorbency, dyeing, printing, antistatic, and anti felting properties. Specialty fabrics, such as with one hydrophilic side and other side hydrophobic could also be produced by UV treatment. On the other hand, fragmentation of a precursor molecule in the plasma zone leads to in situ plasma reaction resulting in the development of pinhole-free hydrophobic textiles. In plasma and UV treatment, as only the surface of the sample is modified, they require a minimum amount of chemicals and energy. In addition, the cost of the final product can also be reduced due to the shorter processing time, exclusion of multistep operations, and partial reduction in effluent treatment. In the plasma- and UV-treated samples, the dyeing time, temperature, and dye bath auxiliaries can be reduced to achieve similar or better depth of shade compared to the untreated sample without compromising the fastness properties.

Keywords Plasma · UV excimer · Textile · Environment-friendly · Surface modification

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1 Introduction

The chemical processing of textiles is important for their improvement in aesthetic and functional value. However, in wet chemical processing of textiles, the industry causes significant water and air pollution during the padding, drying, curing, and post washing operations. Approximately 100 L of water are used to process 1 kg of cotton textile. The cost of the final product also increases due to the multiple numbers of drying operations and effluent treatment. Currently, due to stringent environmental regulations, the textile industry is slowly moving towards implementation of environment-friendly processing technology with a minimal usage of water or without water at all along with usage of eco-friendly chemicals and auxiliaries. This approach will help to develop a sustainable wet chemical processing value chain. In the last two decades, several technological advancements have been demonstrated in textile chemical processing, such as spray and foam finishing, digital printing, and low material-to-liquid processing to reduce the consumption of water and generation of effluents [2, 39]. In addition, present consumers are more conscious of health and hygienic textiles. As a result of this, the demand for cellulosic (cotton) apparel textile processed and finished with natural products such as natural dyes for coloration, enzyme for biopolishing, and neem and aloevera extract for antimicrobial finishing is gaining attention. As far as water conservation is concerned, low-temperature plasma, an emerging technology, can be used for water-free textile processing and finishing by modifying the surface at the nanometer level. Plasma is a partially ionized gas composed of many types of species, such as positive and negative ions, electrons, neutrals, excited molecules, photons, and UV light. It has the potential to be commercialized in textile processing for the development of valued-added home, apparel, and technical textiles at a lower cost, while addressing the problems associated with environmental pollution. Unlike bulk modification of textiles by conventional processes, surface modification of the textile using plasma can be utilized to develop products with minimal usage of chemicals and energy. The surface modification technique is obligated to restrict the modification in the first few atomic layers of the fiber surface, while keeping the bulk properties unaltered. Plasma can exist over a wide range of temperature and pressure. The lightning bolt and the solar corona are examples of plasma present in nature, and as their temperature is quite high (>1,500 °C) they cannot be used for processing of polymeric material. In contrast, cold plasma, also known as low-temperature plasma or nonthermal plasma with bulk temperature of 20–250 °C, can be used for surface modification of polymeric/textile substrates. Plasma is an energetic chemical environment, where the generation of plasma species opens up diverse reactions resulting in various end applications. The surface modification of textiles using plasma can be carried out using non polymerizing gases (small molecule), such as oxygen (O_2), nitrogen (N_2), air, argon (Ar), helium (He), or fluorine (F) for surface activation, cleaning, oxidation, changes in surface energy, increases in surface roughness/area, etching, coating/deposition, and the creation of nanostructures.

These help in improving textile properties in terms of water absorbency, wetting, wicking, oil absorbency, rate of dyeing, adhesion, and antifelting of wool. On the other hand, plasma reaction with a precursor molecule (big molecule) containing vinyl, hydroxyl, carbonyl, carboxyl, acrylate, or fluorocarbon backbone leads to the development of functional textiles, such as hydrophobic, UV protective, antimicrobial, and flame retardant.

Similar to the plasma treatment of textiles, UV excimer lamps have also been explored for similar surface modification. The UV treatment of textiles is also an emerging technology, where surface modification does not involve any in situ polymerization with a liquid or gaseous precursor. However, generation of free radicals by UV treatment followed by graft polymerization of a suitable monomer is possible, and has been carried out for tailor-made surface engineering. It is quite a simple, cost-effective, and dry process, hence it has been explored for surface modification of wool, silk, polyester, and nylon substrate improvement in wetting, wicking, dyeing, antifelting, hydrophilic, and specialty finishing. The UV excimer lamp with 172 nm photons is most commonly used for surface modification of heat-sensitive textile substrates to alter physicochemical properties. Mostly, the textile samples are UV treated in the presence of air, oxygen (O_2), and nitrogen (N_2) gases for surface etching, activation, oxidation, and radical generation.

The present chapter discusses in detail various types of plasma and UV used in wet chemical processing and finishing of textiles with their merits and demerits. Use of these two emerging technologies for the improvement of hydrophilic, oleophilic, dyeing, antistatic, and antifelting of cotton, wool, silk, nylon, and polyester fabrics has been reported in detail. In addition, the use of plasma technology for hydrophobic finishing of textiles using various polymerizable precursors has also been discussed. The advantages of plasma and UV treatments in wet chemical processing of textiles in terms of environmental friendliness and cost-effectiveness in terms of time, temperature, and pollution load have been summarized.

2 Surface Modification of Textiles

Surface modification techniques of polymeric and textile substrates can be classified broadly into two methods, physical and chemical, as discussed below.

2.1 Physical Method

In the physical methods, surface modification of polymer/textile substrates is carried out by either chemically altering the surface of the material or depositing an extraneous layer on the top of the existing material. For the nonreactive precursor, treatment in the presence of high-energy species, for example, radicals, ions, and molecules in excited states helps to generate radicals that on successive reaction produce polar groups. On the other hand, in the second approach, the material surface is superficially coated in the presence of high-energy atoms or clusters of atoms. Different physical techniques of surface modification are discussed below.

(a) *Flame Treatment*
Flame treatment is an old technology and widely used in the printing industry for improving surface hydrophilicity of polyolefin film to enhance printability. Active species such as radicals, ions, and molecules in excited states are formed by high temperature. Distance between the flame and the polymer, number of flames, flame gas composition, temperature, and speed of the machine are adjusted depending upon the material to be processed and functionality required.

(b) *Metallization*
Metallization is the process of coating the polymeric and textile substrate by metal species, deposited by evaporation induced by the Joule effect or electron-beam excitation. The most widespread application is the aluminium coating of plastic films for packaging purposes.

(c) *Sputtering*
The sputtering process involves the creation of ions, accelerating them on a target, and forming atoms or clusters, which are then deposited on the substrates. It is used for producing inorganic coating, when evaporation is not possible. A typical example is ultrathin silver or gold coating of textile/polymeric substrates for scanning electron microscope (SEM) analysis.

(d) *UV Eximer and Laser Treatment*
UV lamps and lasers in the 172–400 nm wavelength are widely used for the treatment of polymer/textile substrates to improve hydrophilic functionality, dye uptake, photon-activated cross-linking of paper coating, and fragmentation of polymer coating.

2.2 Chemical Method

The surface chemical composition of the polymeric/textile substrates can be changed either by direct reaction with a given solution (wet treatment) or by graft polymerization using a suitable monomer. Some of the important chemical methods of surface modification are briefly described below.

2.2.1 Wet Treatment

Wet treatment is the first surface modification technique used in order to improve the surface properties of polymer. For example, hot chromic acid is used to oxidize polyolefin.

2.2.2 Etching

Etching of the polymeric/textile surface is useful for improving adhesion strength. For example, due to the low surface energy of the fluorocarbon, polymers have poor interfacial adhesion strength to any matrix material. The treatment of such polymers using strong reducing agents such as sodium in liquid ammonia improves their interfacial properties due to the etching effect.

2.2.3 Hydrolysis

Among the different hydrolysis techniques, treatment of polyester (PET) by hot sodium hydroxide is the oldest and probably the most exploited method used thus far. This method is used to improve the surface hydrophilicity of the polyester sample.

2.2.4 Grafting

Grafting is achieved by formation of a covalent bond with a molecule on the top of the substrate surface. This is done by first creating radicals on the sample surface by UV/plasma/γ irradiation, followed by grafting polymerization of a vinyl-based monomer.

2.2.5 Plasma Treatment

Plasma, an ionized gas, can be used for surface modification of polymeric/textile substrates by generating polar groups with surface activation, improving surface roughness by plasma etching, and functional properties by plasma polymerization. Therefore, based on the physicochemical changes brought out, the plasma-induced surface modification may be considered either a physical or a chemical method.

3 Generation and Classification of Plasma and UV

Plasma is a partially ionized gas normally generated by electrical breakdown of a gaseous molecule in the presence of high-frequency alternating current (AC) and most commonly used for surface modification of fibrous material. An alternating current with a high-frequency power supply helps in dissociation of various gaseous molecules into a collection of ions, electrons, neutral particles, and other excited species. Plasma is often considered as the fourth state of matter. It was first identified by Sir William Crookes in 1879, and named “plasma” by Irving Langmuir in 1928. Different types of plasmas are discussed below.

3.1 Hot and Cold Plasma

Plasma can be classified into hot/thermal plasma and cold/low-temperature/non-thermal plasma based on the temperature of the plasma zone. Hot plasma occurs when the temperatures of the electrons, atomic and molecular species, are extremely high and remain near to the thermal equilibrium state. In that condition, molecules remain almost fully ionized (100 %). The sun and other stars in various galaxies of the universe, fusion reactors, and plasma torches are examples of hot plasma. In hot plasma, the temperature of the plasma zone is around 10^6–10^8 K with an electron density of $\geq 10^{20}$ m^{-3}. On the other hand, in cold plasma, the electrons remain at a significantly higher temperature, and the ions and neutral molecules remain near to ambient temperature ($T_e \gg T_{ion} \approx T_{gas} = 25$–$250$ °C, $T_{electrons} \approx 727$ °C). In cold plasma, the electron density is significantly lower ($n_e \approx 10^{10}$ m^{-3}) and only a small fraction of gas molecules (~ 1 %) is ionized [42]. Cold plasma is suitable only for surface modification of heat-sensitive polymeric and textile substrates.

3.2 Low and Atmospheric Pressure Plasma

3.2.1 Low Pressure Plasma

It is easy to ionize a gaseous molecule by electrical breakdown under a low-pressure condition, and it has been extensively studied for material processing. The advantages of low-pressure plasma processing are: (i) presence of a high concentration of reactive species, (ii) uniform glow plasma, (iii) temperature of plasma below 250 °C, and (iv) lower breakdown voltages. However, some of the limitations of low-pressure plasma processing are: (i) longer processing time, (ii) limited sample size to the size of the reactor, and (iii) mostly batch processing.

3.2.2 Atmospheric Pressure Plasma

Unlike low-pressure plasma, it is quite challenging to generate plasma at atmospheric pressure due to the presence of high voltage in a narrow electrode gap and the difficulty in ionizing gaseous molecules and generation of uniform cold plasma. However, if the stable cold plasma can be generated at atmospheric pressure, it can overcome the limitations of low-pressure technology. It can also be easily integrated into existing textile processes for continuous treatment of textiles. The three major types of atmospheric pressure cold plasma commonly used in textile processing are briefly discussed below.

(a) *Dielectric Barrier Discharge*
The dielectric barrier discharge provides a strong thermodynamic non equilibrium plasma at atmospheric pressure with a moderate gas temperature. It is produced by an arrangement consisting of two parallel flat electrodes. Among them, at least one electrode is covered with a dielectric plate. An AC voltage in the range of 1–100 kV with a RF frequency of 50 Hz–100 kHz is applied to ignite the DBD plasma. The textile sample is kept between the two electrodes having a gap of <1 mm to several mm, and gas or a mixture of gases is then injected for uniform treatment of the textile. The DBD plasma is used in plasma-assisted chemical vapor deposition, surface etching, surface cleaning, surface activation, and plasma polymerization.

(b) *Corona Discharge*
Corona discharge is the characteristic of an asymmetric electrode pair either powered by a continuous or pulsed by an AC/DC electrical supply. In a highly nonuniform electric field such as a point, plane gap, or wire cylindrical gap, when the high electric field near the point electrode exceeds the breakdown strength of a gas, plasma is formed. The plasma discharge gap is kept at about 0.5–2 mm. The corona discharge is used in electrostatic precipitators in dust collection and activation of polymer/textile substrates to improve the hydrophilic property.

(c) *Plasma Jet*
The atmospheric pressure plasma jet (AAPJ) consists of two concentric electrodes through which a flow of a mixture of gases is supplied. The inner electrode is coupled with 13.56 MHz or kHz RF power with a discharge voltage in the range of 250 V to 10 kV, and the outer electrode is grounded. The discharge is ignited by a RF power between the outer and the inner electrodes, thus producing a high velocity of highly reactive species for the downstream processing of textiles.

3.3 UV Treatment

Surface modification such as etching, ablation, deposition, and evaporation by laser treatment can be carried out in various ways depending on the purpose of such modification. A large number of lasers are capable of operating at different wavelengths, and different modes are available for the surface modification of various substrates. The operating principle is based on the radiative decomposition of excimer states created by a silent discharge in a high-pressure gas column. A typical lamp consists of two concentric quartz tubes, outer and inner metallic electrodes with a discharge gap of a few millimeters, and an external high-voltage generator. The discharge gap is filled with either a rare gas or a rare gas-halogen mixture. The photons are emitted through the quartz wall, which is transparent to the generated radiation. An alternative high voltage of 7–10 kV and frequency of

50 Hz to several MHz is adequate to run the arc discharge between the electrodes. The charge buildup on the dielectric surface immediately decreases the field in the discharge gap and extinguishes the arc [24]. Excimer lamps are used for surface modification of polymers and textile substrates for improving in antimicrobial, antisoiling, antifelting, antistatic, wettability, adhesion strength, and cross-linking properties.

3.3.1 Excimer Laser

Lasers, which use noble gas for laser generation, are generally referred to as excimer lasers. They operate in the ultraviolet to near UV region, that is, from 193 to 351 nm. For instance, CO_2 and Nd: YAG lasers are the most powerful, however, they are not suitable for modification of polymeric substrates because of their longer wavelength and lower photon energies, insufficient to break the molecular bonds of polymers. Excimer lasers, however, are capable of operating in the UV region and are strongly absorbed by the polymers for photochemical reaction. It is difficult to expose large areas of polymers in an efficient way due to the requirement of a large and quite expensive facility [64].

3.3.2 Excimer Lamps

The term *excimer* stands for “excited dimmer.” Excimers, which exist only in the excited state and under normal condition, do not possess a stable ground state. The excimer molecules are not very stable and once formed, within a few nanoseconds give up their excitation energy in the form of UV photons. UV lamps work on the dielectric barrier discharge principle and emit intense monochromatic light in the UV region of the spectrum. Organic materials, which have nonbonding electron pairs, strongly absorb light with a wavelength shorter than 200 nm. The penetration depth of a photon is approximately 10 nm. The bond dissociation power of the photon is different for the various excimer systems. For example, if xenon gas is used, it emits 172 nm light, which corresponds to photon energy of 7.2 eV that is capable of breaking polymeric bonds, such as C–H, –C=O, and –OH.

4 Environment-Friendly Textile Processing Using Plasma and UV

It is well known that during the wet chemical processing of textiles, industries consume a large quantity of water and generate a similar amount of effluent. The cost of final products also increases due to the multiple numbers of drying operations. Recently, due to the increase in environmental awareness and effluent

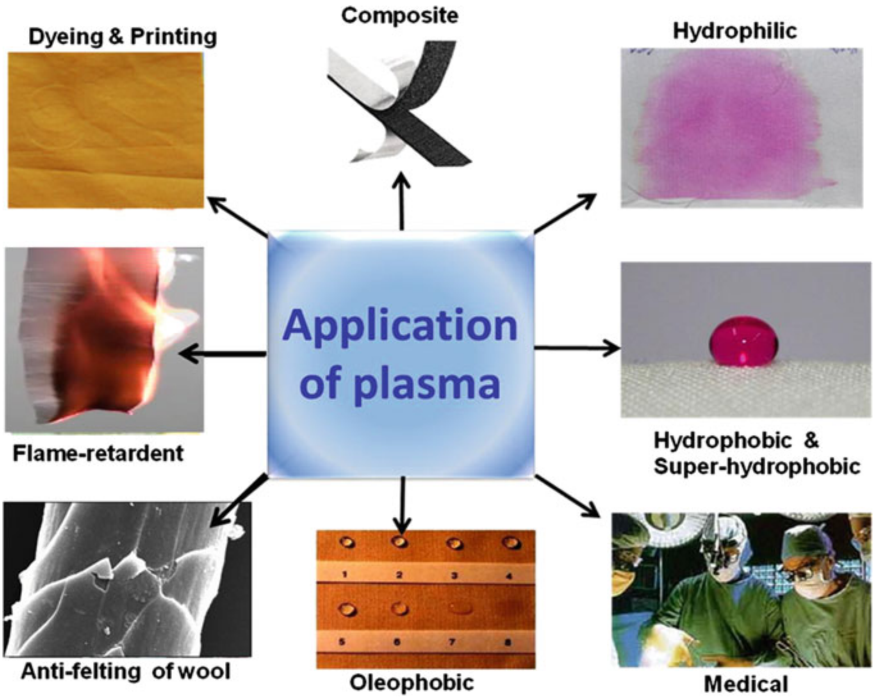


Fig. 1 Application of plasma for textile processing and finishing

norms, textile industries are slowly moving towards the implementation of environment-friendly low-water-based technologies, such as digital printing, spray, foam finishing, supercritical fluids, and solvent processing for the development of sustainable textiles. The industry is also using eco-friendly chemicals and agents such as natural dyes, enzymes, and plant extracts for textile processing and finishing, while avoiding usage of hazardous to nonhazardous chemicals to develop green/eco-textiles. In this context, cold plasma and UV treatment seem to be promising environmentally friendly technologies for the wet chemical processing of textiles. Plasma treatment of textiles modifies only the surface of the material without altering the bulk properties to increase the uptake of dyes and chemicals or to impart a unique functionality or both. Different value-added functionalities, such as water, stain and oil repellent, hydrophilic, antimicrobial, flame-retardant, UV-protective, antistatic properties, and improvements in dyeing, printing, biocompatibility, and adhesion can be accomplished by modifying the fiber surface at the nanometer level as shown in Fig. 1. The main advantages of plasma processing of textiles are (i) liquid-free dry single-step operation, (ii) requirement of a minimal amount of chemicals, (iii) cost-effectiveness in terms of time and temperature, (iv) imparted functionality independent of substrate chemistry, and (v) environmental friendliness. Low-pressure plasma has been extensively studied for such applications, but the process technology has not been commercialized in textiles due to its inherent technoeconomical limitation. On the other hand, atmospheric-pressure cold plasma can overcome the limitations of low-pressure plasma technology and is being explored for similar applications. Hence, it is becoming popular both in research as well as commercial applications in textile and allied sectors. Atmospheric pressure plasma is an emerging technology and several challenges associated with plasma generation for in situ plasma reactions with textile substrates are still not fully addressed for their inline integration with existing textile processes.

Surface modification with a desired functionality could be achieved by selecting the appropriate plasma process parameters along with a suitable precursor molecule. Fragmentation of a precursor followed by plasma reaction with textile substrates is the best way of surface engineering to develop value-added technical, apparel, smart, and home textiles. Similar to plasma processing of textiles, UV treatment can also be used for increasing surface area, hydrophilic property, antifelting, antistatic, dyeing, printing, and adhesion strength. In both processes, there is no requirement of any prior treatment, such as swelling the fibers in organic, aqueous, or alkaline solvents. The changes in properties induced by plasma and UV treatment are therefore restricted to the surface only. From the physical point of view, roughening of the fiber surface is responsible for changes in coefficient of friction, top cohesion, spinnability, yarn strength, and increase in antifelting of wool. From the chemical point of view, fiber surface oxidation and reaction with suitable precursor molecules are the main factors responsible for improving the various functional properties of textiles. The comparison of textile processing by conventional method, plasma treatment, and UV treatment is summarized in Table 1.

In comparison to UV treatment, plasma technology has an additional advantage of surface modification by in situ plasma coating, deposition, and polymerization. Plasma chemistry is a complex process that involves a large number of elementary homogeneous and heterogeneous reactions. The homogeneous reaction occurs between species in the gaseous phases and the heterogeneous reaction between the plasma species and solid surface. In UV treatment, UV excimers exist only in the excited dimer state and give up excitation energy in the form of UV photons (monochromatic light). The highly energized UV photon of shorter wavelength (<200 nm) could modify the fiber surface by approximately 10 nm. The energy of the photon depends upon the gases used to generate, for example, xenon gas (172 nm) has a photon energy of 7.2 eV and mercury (185.9 and 253.7 nm) also has similar energy capable of physical changes, such as etching, roughening, and increasing surface area and chemical changes, including breaking the chemical bond (C–H, –C=O, –OH) and generation of polar groups (C=O, –COOH, and NH_2) depending upon the UV irradiation time and atmosphere used [4]. Different types of interaction of plasma and UV with substrates are discussed below.

Table 1 The Comparison of textile process using conventional method, plasma, and UV treatment

Different parameters	Conventional wet chemical processing of textiles	Plasma processing of textiles	UV treatment of textiles
Processing medium	Liquid-based (mostly water)	Ionized gas and no need of water	Energy of the UV photon and no need of water
Water requirement	Approximately, 100 l/kg of cotton textile for complete wet processing	Zero for a particular processing	Zero for a particular processing
Dyeing time, temperature, and consumption of dye	Conventionally most textile dyeing is carried out at boiling temperature	Dyeing temperature can be reduced. Similarly, dyeing time can be reduced up to 30 min to achieve similar dye exhaustion. Furthermore, the plasma-treated sample shows more exhaustion resulting in less coloring material present in the effluent liquid	Dyeing temperature can be reduced. Dyeing time can be reduced up to 50 min to achieve similar exhaustion. The UV-treated sample shows more dye exhaustion resulting in less coloring material present in the effluent liquid
Dye bath auxiliaries	There is a need for acid, alkali, salt, etc. resulting more effluent load	In dyeing of many fibers usage of acid, alkali, or salt may be reduced or avoided resulting in a less effluent load	Similar or better than the conventional process
Time required for textile processing/finishing	More, due to the multistep operation, e.g., 10–20 min required for hydrophobic finishing	Less, as multistep processes can be accomplished in a single step. For example, hydrophobic finishing can be completed in 1–10 min	Time of hydrophilic finishing can be reduced
Energy requirement	High due to the involvement of drying/curing of wet textile	Energy effective as it is a single-step water-free dry process	Energy effective as it is a water-free dry process
Consumption of chemicals	High as it is bulk modification of textile	Low as surface of the textile is only modified	Low as surface of the textile is only modified

(continued)

Table 1 (continued)

Different parameters	Conventional wet chemical processing of textiles	Plasma processing of textiles	UV treatment of textiles
Cost of production	High due to the requirement of more chemicals and longer processing time	Low due to the requirement of fewer chemicals and rapid processing	Low due to the requirement of fewer chemicals
Sustainability in terms of chemicals, cost, energy, and pollution	Less, as the process uses many nontoxic to toxic chemicals along with the water and energy-intensive process	More, as mostly nontoxic gases, such as air, nitrogen, oxygen, helium, and argon are used. In this process, the requirement of chemicals, energy, and water is less than the conventional process	More, as the process uses only energy of the UV photon along with the inert gases. In this process, the requirement of chemicals, energy, and water is less than the conventional process

(i) *Ion formation*: Reactions due to the ion formation that would directly lead to a new chemical product, such as formation of NH_3 and NO_2.
(ii) *Recombination*: When the rate of producing surface radicals is high and air is excluded, a tough cross-linked shell is formed that offers protection against solvent attack.
(iii) *Oxidation*: In treatment by oxygen containing plasma/UV, surface excitation leads to the formation of polar groups, such as ketone, hydroxyl, ether, peroxide, and carboxylic acid that make the surface wettable.
(iv) *Peroxide formation*: When a textile is exposed to argon (Ar) plasma followed by exposure to air, a high proportion of reactive sites is converted to peroxide form. Because peroxide is known to act as an initiator for vinyl polymerization, it is used for graft polymerization.
(v) *Radical formation*: Carbon-free radicals are formed when the energetic ions/photons from the plasma/UV break the organic bonds of the polymeric substrate.
(vi) *Polymerization*: Ionization of an organic monomer in the vapor phase in the plasma zone leads to a rapid in situ polymerization resulting in formation of thin pinhole-free films.
(vii) *Surface cleaning*: A cleaning process in which argon (Ar), helium (He), and oxygen (O_2) gases are used to ablate organic contaminants such as oil from the substrate surface.

5 Improvement on Liquid Absorbency

5.1 Improvement in Water Absorbency

5.1.1 Plasma Treatment of Textile

The effect of atmospheric pressure glow (APG) cold plasma in the improvement of the hydrophilic property in terms of water absorbency time was measured in nylon and polyester woven fabrics [53–55]. The samples were helium (He) plasma treated in an indigenously developed plasma reactor in a continuous manner. Water absorbency was measured according to the AATCC test 39-1971 method by putting a 37 μl distilled water droplet on the fabric. It was observed that a water droplet took 540 s to spread over an area of 3.79 cm^2 in the untreated nylon sample, whereas it took only 1.1 s in the 60 s He-plasma–treated sample. In the polyester (PET) sample, the water absorbency time was found to reduce from 700 to 6.7 s in the untreated and 60 s He-plasma–treated samples, respectively. Absorption and spreading of water was very slow in the untreated sample because of the absence of polar groups in the polymer backbone. However, after plasma treatment, the surface energy of the samples increased significantly, probably due to the generation of hydrophilic groups. Surface energy of the as-procured nylon fabric was below 43.4 $milliJ/m^2$ and after 60 s of plasma treatment, it was found to increase to 63 $milliJ/m^2$ in the He, argon (Ar), or air–plasma treated samples. In the polyester sample, the surface energy was found to increase from 36 $milliJ/m^2$ in the untreated sample to the maximum measurable value of 71 $milliJ/m^2$ in the plasma-treated sample. The normalized peak intensity of $–NH_2$ groups in the nylon sample increased significantly from 1.261 for the untreated sample to 1.409 and 1.428 for the 60 s air and He plasma-treated samples, respectively. In the air–plasma treated sample, there was a small increase in 1,633 cm^{-1} (–CONH–) peak as well. The small increase in the value of the normalized peak intensity for the –C=O group in the polyester sample could have happened due to the formation of more –COOH groups. The chemical changes in the plasma-treated nylon samples were found to be more profound than the plasma-treated polyester samples. The changes measured in ATR-FTIR analysis were marginal due to their low sensitivity to nanoscale analysis. Scanning electron microscope (SEM) and atomic force microscope (AFM) images of the plasma-treated samples showed significant improvement in surface area and surface capillaries, which might have helped in faster wetting and wicking of the samples. Therefore, it was concluded that the faster water absorbency in the plasma-treated samples was due to the cumulative action of nanosized channel's (capillary action) formation and increase in surface energy due to the formation of polar groups. Samanta in [52] studied plasma treatment of polyamide 6 (nylon 6) woven textiles in a continuous manner for 10, 15, 30, and 60 s in helium (He) and a helium–oxygen ($He–O_2$) mixture. The samples were exposed to air after the plasma treatment to allow the formation of various polar groups. In the untreated nylon sample, a water droplet of 37 μL did

Table 2 Water absorbency time in the untreated, He, and He–O_2 Plasma-treated samples

Plasma treatment time (s)	Water absorbency time (min)	
	He plasma	He–O_2 plasma
0 (Untreated)	>60	>60
10	>60	>60
15	35.3	9.1
30	3.5	0.08
60	0.08	0.05

not get absorbed by the fabric even after 60 min (maximum measured time). After plasma treatment of 10 s, there was no improvement in the water absorbency time (Table 2). However, after 15 s of plasma treatment, there was an improvement in hydrophilic functionality. As a result of the same, the water absorbency time was found to reduce from >60 min in the untreated sample to 9.1 min in the He–O_2 and 35.3 min in the He plasma-treated samples.

With increasing plasma treatment time to 30 s, the water absorbency time further reduced to 0.08 and 3.5 min for the He–O_2 and He plasma-treated samples, respectively. The 60 s plasma-treated sample showed an excellent hydrophilic property with water absorbency time of 0.05 min (3.3 s) and 0.08 min (4.9 s) in the He–O_2 and He plasma-treated samples, respectively, as shown in Fig. 2.

In the both 30 s He and He–O_2 plasma-treated samples the water contact angle was found to be ~0°, whereas in the untreated sample it was as high as 130°. It was interesting to note that the He–O_2 plasma treatment was more effective in improving the hydrophilic property compared to the He plasma treatment. This may be due to the formation of more oxygen-containing hydrophilic groups in the presence of oxygen in He–O_2 plasma. Furthermore, it was observed that the imparted hydrophilic functionality in nylon fabric was durable to heat treatment at 70, 90, and 110 °C for a prolonged time and it can also be stored for more than 6 months. Similarly, it has been observed that the surface energy of the melt-blown nylon could be increased to 70 dynes/cm within 5 s of the glow plasma treatment. The imparted hydrophilic functionality was durable up to 6 months. Thereafter, surface energy reduced from 70 to 64 dynes/cm after 1 year of ageing in atmospheric condition [67].

The surface chemistry of both the untreated and plasma-treated samples were analyzed using X-ray photoelectron spectroscopy (XPS) to reveal the change in atomic percentage in different samples. In the untreated sample, the surface oxygen percentage was 18.6 % and it increased significantly to 21.8 % in the 60 s He plasma-treated and 29 % in the He–O_2 plasma-treated samples. The increase in surface oxygen might have helped in formation of more oxygen-containing polar groups, such as ketone, hydroxyl, ether, peroxide, and carboxylic acid. In the plasma-treated samples, the surface nitrogen percentage was a little lower compared to the untreated sample. Surface molecules in both the untreated and plasma-treated samples were also analyzed using a secondary ion mass spectrometer (Model: MiniSIMS, Millbrook Company, UK). The untreated sample showed the

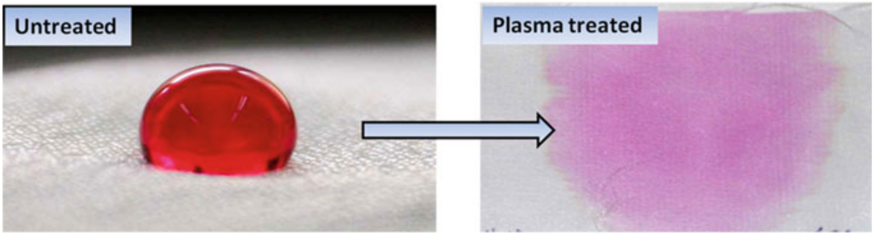


Fig. 2 Conversion of hydrophobic nylon to hydrophilic upon He–O_2 plasma treatment [52]

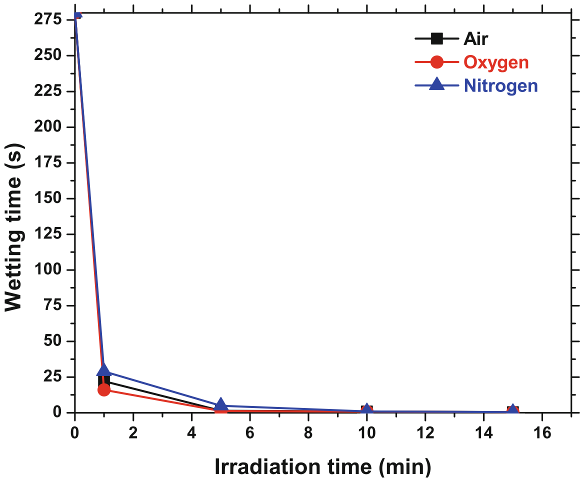
presence of major fragments of nylon at different masses, such as 13 amu for CH^-, 16 amu for O^-, and 17 amu for OH^-. In addition, other mass peaks were C^- at 12 amu, $CH_2{}^-$ or N^- at 14 amu, C–C^- at 24 amu, and CH−C^- at 25 amu, and CH−CH^- at 26 amu. The presence of these masses in the untreated sample is an indication that during the SIMS analysis major bonds of nylon, such as $-CH_2-CH_2, -CO-NH-$ and so on were broken down into smaller molecules and atoms, such as C^-, CH^-, CH_2^-, N^-, O^-, HO^-, $C-C^-$, and $C-CH^-$. In the plasma-treated samples similar mass patterns were also observed. In the untreated sample, the peak intensity for OH^- at 17 amu was smaller than the CH^- peak at 13 amu. However, in the plasma-treated samples, the HO^- peak intensity was more than that found with CH^- at 13 amu. It was seen that in the untreated sample the O^-/CH^- ratio was 2.4 and it increased to 2.7 and 3.0 in the He and He–O_2 plasma-treated samples, respectively. The O^-/N^- ratio in the untreated sample was 9.2 and it increased to 14.0 and 16.9 in the He and He–O_2 plasma-treated samples, respectively. The result indicates that both plasma treatments followed by exposure of samples in air might have helped in formation of polar groups. The SEM of the untreated nylon sample showed smooth surface morphology. However, after treatment in He plasma very regular particulate type surface features were observed and these special features became even more dense when the sample was subjected to He–O_2 plasma treatment. Such changes on the fiber surface might have resulted from plasma-enhanced surface etching. The changes in physical and chemical properties jointly have contributed to the improvement of the water absorbency of textiles.

Similarly the effect of He, He–O_2 and He–maleic anhydride (He–MA) treatment on polyester fabric was used to study the effectiveness of different plasma for hydrophilic surface modification [45]. Different plasma parameters such as discharge voltage, frequency, and time of treatment were varied to study their individual effect on the hydrophilic property. During the plasma treatment, frequencies were kept at 19, 20, and 22 kHz and time of treatment was varied in the range of 0.5–5 min. It was seen that a water drop took 2,100 s to be fully absorbed by the hydrophobic polyester fabric. However, when the sample was He plasma-treated for 0.5 min, water absorbency time reduced to 478 s ($V = 2.36$, $F = 19$) and further to 145 s in the 5 min plasma-treated sample. With increasing He plasma treatment time, the water absorbency time also reduced. As discussed above for nylon samples, the He–O_2 (He 1,500 ml/min, O_2 350 ml/min) plasma-treated samples showed better absorbency time compared to the He plasma samples for the polyester samples also. In those samples, the water absorbency time was found to reduce from 252 s for the 0.5 min plasma-treated sample to 85 s for the 5 min plasma-treated sample. It was also seen that plasma treatment at lower frequency could impart better hydrophilic functionality. On the other hand, when the polyester fabric was first padded with maleic anhydride solution followed by plasma treatment in He at 19 kHz and 2.36 kV for 5 min, the sample showed minimum water absorbency time of 99 s. The imparted hydrophilic functionality was durable to storage time and number of washing cycles. Yet in an another study, the atmospheric pressure plasma with He–Ar or acetone–argon on wool and polyester (PET) fabrics were carried out and it was found that wettability increases with increasing plasma treatment time. Plasma treatment by He–Ar was found to have more effectiveness than the acetone–argon plasma [72]. Low-pressure plasma treatments using oxygen containing gaseous mixtures (Ar–O_2 and He–O_2) on polyester fabric, improved wettability significantly due to the formation of polar groups on the surface. The imparted hydrophilicity also depends on the fabric structure, such as a better result in a loose fabric structure compared to tightly woven fabric [20]. As indicated above, the atmospheric pressure air plasma treatment (300–1,000 W) of PET woven fabric improves surface energy and reduces the water contact angle and water wicking time. The weight of water absorbed by the capillary increased from 12 to 200 mg. The water contact angle on the plasma-treated PET sample decreased from 80 to 40° due to the chemical change of the fiber surface [14]. The wettability of polyester can be improved with a simultaneous decrease in soiling property by corona treatment in air. During plasma treatment, fabrics accumulate a negative charge and soils are also negatively charged and hence, they repel each other keeping the fabric free from soil. Plasma etching also increases the hydrophilic characteristic that also decreases soiling [75]. Atmospheric-pressure plasma treatment of polypropylene nonwovens with nitrogen and dry air resulted in surface activation and permanent hydrophilic functionalization of lightweight nonwovens. Similarly, with acetylene mixed with ammonia plasma (C_2H_2/NH_3) treatment of textile improves wettability slightly [18].

The objectives of increasing hydrophilic features and reducing chemical waste from existing pretreatment processes for cotton fabrics were achieved by corona discharge in an air atmosphere [17]. It effectively increased the hydrophilic property without affecting the integrity of the fiber or yarn. The treatment causes chemical and physical changes in the waxy cuticle layer of the cotton without damaging the cellulose backbone. Pectinase enzyme treatment subsequent to air or Ar plasma treatment was applied in linen fabric preparation. Alkaline treatment was most effective in removing the hydrophobic outer layer of raw linen to give a wetting time of 10 ± 1 s. Argon–plasma-treated linen showed less wetting time (80 s) than the air–plasma treated one (100 s) indicating formation of polar species on the raw linen fabric. Air or argon–plasma pretreatment followed by Beisol PRO enzyme application can reduce the wetting times significantly to 20 and 16 s, respectively. Exposing the linen fabrics to either plasma or enzyme treatment causes a significant increase in the wetting rate and with a combination of argon–plasma treatment with Beisol PRO enzyme was the most effective next to alkaline scouring. Alkaline scoured, argon plasma treated, argon plasma followed by Beisol PRO enzyme treatment, or Sera-Zyme C-PE treatment was characterized by the highest total surface free energy values of 26.08, 26.40, 25.83, and 25.82 mJ/m^2, respectively, compared to 21.89 mJ/m^2 for untreated linen. Polyester/cotton (P/C) blended woven textile was treated with DBD plasma to improve hydrophilic properties using He–O_2 gases [25]. It was found that plasma process parameters played a critical role in deciding the efficiency of the treatment, and at optimum conditions, the hydrophilicity in terms of vertical wicking was found to be higher than the untreated sample. Polyester has a hydrophobic surface as it is made up of ether oxygen (C–O–C) linkages, where the hydrophilic ester oxygen (C=O) linkages are facing towards the core of the fiber. When the sample was plasma treated, the ester oxygen (C=O) coming closer to the surface as a result of etching or formation of new C=O bonds, helped the sample to be more hydrophilic [35].

Atmospheric pressure plasma has also been used for surface modification of protein fiber, such as wool to improve wettability [44]. After the plasma treatment, the water absorption time decreased from >3,600 s in the untreated sample to <1 s in the helium–plasma treated sample. The change in wettability in protein fabric is likely because of the removal of a covalently bound fatty acid layer from the surface. This exposes the underlying hydrophilic protein material along with the generation of additional polar groups. As a result of this, there was an increase in the intensity of HO^- and NH^- groups in SIMS analysis. In the untreated sample, the intensity of the CH^- peak was very high compared to HO^- and NH_2^- peaks probably due to the presence of a fatty acid layer on the wool cuticle. In the plasma-treated sample, the intensity of the CH^- peak reduced significantly and intensities of HO^- and NH_2^- peaks increased profoundly. There was no detectable ageing effect of improved hydrophilic property after 9 weeks of storage and 30 wash cycles. Wool was also made highly hydrophilic by a different plasma treatment, as a result of the wetting time being reduced from 900 s in the untreated sample to less than 1 s in the plasma-treated sample [31]. The possible reason for this is the removal of the hydrophobic epicuticle of wool fiber and formation of cysteic acid from cystine. The improvement in the hydrophilic property and/or surface area/roughness was utilized for improvement in dyeing and antifelting of wool. The wettability in terms of water absorption time in the 5 min N_2 plasma-treated fabric decreased from 180 to 1 s in the untreated sample. Similar results were also observed when the sample was plasma treated in O_2 plasma. Upon plasma treatment, various physicochemical changes were observed in wool, such as (i) additional formation of –C=O, –OH, –COOH groups, (ii) slight improvement in crystallinity, and (iii) increase in surface area. It has been observed that on 5 min of O_2 plasma treatment, the C percentage decreased by 12 % (XPS analysis). On the other hand, the N and O percentage increased by 1 and 48 %, respectively, due to formation of more –C=O, –OH, and –COOH groups on the surface. Similar to N_2 plasma treatment, the reduction in sulphur (S) percentage was also noted in the O_2 plasma-treated sample. In the O_2 and N_2 plasma-treated

Fig. 3 Effect of UV excimer irradiation time on wetting of wool fabrics [4]



samples, the C/N decreased and the O/C ratio increased [30]. Plasma treatment was found to improve the wettability of degummed silk fabric. Similar to plasma treatment of wool as discussed above, 5 min O_2 plasma-treated Tussar silk fabric showed a wicking height of 100 mm in ~5 min, whereas in the control silk the maximum height of 100 mm was observed after a prolonged time. In the Eri and Muga silk, the plasma treatment nearly doubled the wicking rate compared to the untreated silk. ATR-FTIR spectra showed an increase in β-sheet structure after 15 min of O_2 plasma treatment and disappearance of the silk amide-II random coil band. However, the amide-II random coil band was observed if the characterization could be carried out within few hours of plasma treatment. It might be due to the formation of the β-sheet from amide-II because of surface ageing [76]. Unlike the hydrogen (H_2) plasma treatment, the O/C and N/C atomic ratios improved slightly after O_2 and N_2 plasma treatment. The effect of NH_3 plasma on silk has also been studied and was found to improve the N atomic percentage considerably.

5.1.2 UV Treatment of Textiles

Similar to plasma treatment of textiles, UV treatment has also been explored for surface modification of natural as well as synthetic textiles to improve hydrophilic functionality. The wool fabric surface was modified using a Xenon Excimer UV lamp, that has almost monochromatic light in VUV region ($\lambda = 172$ nm) with irradiation power of 50 mW/cm^2 [4]. It can be seen from Fig. 3 that the untreated scoured wool fabric has a high wetting time of 280 s due to the presence of many hydrophobic molecules on the surface. However, similar to plasma treatment, after UV irradiation in an air atmosphere, the sample became highly hydrophilic. As result of this, wetting time reduced to 22.2 and 1.5 s in the 1 and 5 min treated samples, respectively.

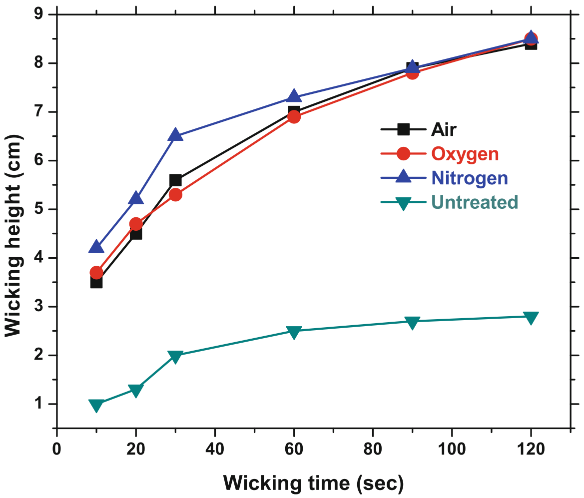


Fig. 4 Vertical wicking in the untreated and 15 min irradiated wool fabrics [3]

It can be seen from Fig. 3 that with increasing irradiation time, the wetting time initially decreases exponentially and later on linearly. The 15 min treated sample showed the lowest wetting time of 0.5 s. Similar trends were also observed when the samples were treated in the presence of O_2 and N_2 atmosphere. The wetting time in the nitrogen (N_2) -treated sample was a little higher compared to air and O_2 treated samples. This is because the presence of oxygen helped in formation of the polar group that assisted in wetting. It can be seen that 1–5 min of UV irradiation is sufficient to impart a high degree of hydrophilic functionality in wool fabrics. The improvement of the hydrophilic characteristic of wool fabric upon UV exposure is attributed to (i) removal/modification of the fatty lipid layer on the fiber surface, (ii) cleavage of disulphide protein linkages (–S–S–) to produce sulphonic acid groups ($–SO_3H$) due to the presence of oxygen, and (iii) formation of oxygen-rich polar groups on pertinacious/lipid carbon sites. Wool fiber is characterized by the hydrophilic core protected by the fatty waxy hydrophobic thin film (0.9 nm) on the outer epicuticular layer. This layer does not get removed even after an alkaline scouring and to the contrary, acts as a barrier for penetration of water and dye molecules. UV excimer treatment reduces the wetting time by a factor of 10, even after 1 min of exposure, irrespective of the nature of atmosphere used.

Similar to wetting time, vertical wicking in the 1, 5, 10, and 15 min UV irradiated samples in air, O_2 and N_2 atmosphere was evaluated with a rectangular piece of fabric (100 mm × 20 mm). As wetting and wicking are the two interrelated phenomena, a liquid does not wick well until and unless it is truly wettable. It can be seen from Fig. 4 that the untreated sample has a very low rate of water wicking. However, upon 15 min of UV irradiation, the wicking rate increased significantly. It was found that irradiation beyond 15 min does not show further improvement in wicking. The irradiation in a nitrogen atmosphere showed the best result compared to the air- and oxygen-treated samples. It may be due to the formation of more striations in the N_2 atmosphere. The observed wicking behavior can be explained with reference to the capillary action of water, which is defined as the upward movement of water against the gravitational force within the spaces of a porous material. The irradiation of wool by UV damages the fatty layer and develops hydrophilic groups on the surface. This phenomenon contributed positively to the adhesive forces between the fiber and water molecules, leading to an increase in wickability [62]. In addition, the effective striations present in the UV-treated wool fabric might have increased resulting in increasing the wickability.

The UV-treated wool fabric took only 10 s to travel a height of 2 cm irrespective of atmosphere used in comparison to 2 min required in the untreated sample [6]. The high-energy UV photon etched the wool fabric surface, broke its waxy smooth scales, and created a capillary as observed under the SEM. Oxygen incorporation in the treated fabric surface by the ozone mechanism was proposed by Basak in [3]. Surface oxidation of disulphide protein linkages (–S–S–) of wool produced sulphonic acid ($–SO_3H$), removed the surface fatty waxy layer, and formed extra polar groups, such as C=O, –COOH, and $–NH_2$ [6, 15]. All these factors together helped in better wetting and wicking. Periyasamy et al. in [46] reported that 172 nm UV excimer treatment of silk fabrics could improve the wetting and wicking properties. It might be due to the increased surface roughness and formation of nano pores in the treated fabric. The wettability of polyester fabric was improved using a UV excimer lamp, emitting mostly monochromatic light of 172 nm with an irradiation power of 50 mW/cm^2. The samples were irradiated for 1, 3, 5, and 10 min keeping 5 mm distance from the lamp. The high-energy photon (7.2 eV) is capable of breaking even a C=C bond, leading to the generation of free radicals. The polyester samples previously equilibrated with the surrounding atmospheric gases (air) contain a quantity of dissolved oxygen, particularly on the superficial layer. The diffused or ambient oxygen quickly reacts with these free radicals producing oxidized molecules, such as ketone, carboxylic acid, alcohol, and peroxide species. In the UV-treated hydrophilic polyester fabric, the wetting time was significantly reduced from 6.7 (untreated) to 3.1 s and wicking time from 100 (untreated) to 65 s. The effect intensifies with an increase in irradiation time. The improvement in wetting and wicking is attributed to the creation of oxygen-rich species and submicron-level surface roughness. There was no significant change in the crystallinity and tensile strength as UV treatment only renders change in the surface of the fibers.

5.2 Improvement in Oil Absorbency

The atmospheric pressure glow plasma was generated in the presence of helium (He), argon (Ar), oxygen (O_2), and air gases to improve oil absorbency in the various textile substrates [54]. A drop of 37 μl of mustard oil was placed on the fabric, and the time was measured to spread over an area of 3.79 cm^2. For cotton, three oil drops were placed simultaneously, as one drop of oil was found insufficient to spread over the specified area. In all the plasma-treated samples, there was a significant improvement in oil absorbency. In the nylon sample case, the oil spreading time decreased from 152 to 52 s in the untreated to 60 s He plasma-treated samples. Similar results were also found when the samples were plasma treated in the presence of Ar, O_2, and Air gases. Air plasma-treated samples took slightly more time (75 s) compared to the helium plasma-treated sample (52 s). Plasma treatment helped to reduce the oil spreading time approximately by half to one third compared to the untreated sample. Similar to nylon, the oil spreading time in polyester woven fabrics was found to decrease from 28.6 min in the untreated sample to 2.8 min in the 60 s He plasma-treated sample. It was interesting to note that in the plasma-treated sample, the rate of oil absorption and spreading was more, although the sample turned from hydrophobic to hydrophilic. Furthermore, even on the highly hydrophilic cotton textile, oil (hydrophobic liquid) spreading time decreased from 59.5 s in the untreated sample to 30.4 s in the 60 s He plasma-treated sample. Similar results were also observed in air, Ar, and O_2 plasma-treated samples. The SEM pictures at a magnification of 35 KX revealed the surface features of <100 nm due to the formation of hills and valleys. The AFM micrograph of the untreated samples over an area of 4 μm × 4 μm (Z-axis 500 nm/div) appeared to have a smooth surface. After the plasma treatment, vertical channel-like features with dimensions of <200 nm were easily visible in the nylon sample due to the bombardment of high-energy plasma species. In the plasma-treated polyester sample, horizontal channel-like features of ~100 nm in height and separated from each other by about 350 nm in the horizontal direction were easily visible (Z-axis 200 nm/div). In both the plasma-treated samples, nanosized horizontal and vertical channels were uniformly distributed over the entire surface area. The formation of such channels upon plasma treatment increased the effective capillary radius resulting in better fluid spreading. In the untreated cotton textile, better oil absorption was due to the presence of a textured and convoluted structure, and on plasma treatment these features might have enhanced, resulting in further improvement in oil absorbency. Cotton has more surface energy than the oil, hence oil could spread easily. Upon plasma treatment, the surface energy might have enhanced further. Also formation of pores, micro-cracks, and an increase in surface roughness in the plasma-treated cotton might have also helped in better fluid transport. Improvement in oil absorbency of textile substrates would have possible applications in cleaning of surfaces contaminated with oil in the metal industry, household cleansers, and cosmetics.

The UV eximer has also been used similarly to the plasma treatment of textiles. It was found that oil spreading time was much lower in the untreated wool fabric than the water spread time [3]. This is because for spreading of any liquid on a solid surface, the surface energy of the solid surface must be equal or more than the surface energy of the liquid. Due to the presence of a hydrophobic fatty layer on the wool fiber surface, it has low surface energy, similar to surface energy of oil. As a result, oil could spread easily in the untreated sample. However, water has a surface energy of 71 dynes/cm, which is much more than the surface energy of wool, and as a result of this, water did not get absorbed/spread by the untreated sample. After UV irradiation, surface energy of the wool fabrics increased due to the generation of polar groups and increased in surface roughness resulting in faster spreading of oil and water also (as discussed above). The oil spreading time decreased from 2.7 s in the untreated sample to 0.5 s in the 15 min UV irradiated samples. With increasing irradiation time, the oil spreading time was found to decrease further. Air and O_2 irradiated samples showed similar results, however, the N_2-treated sample showed a slightly better result.

6 Improvement in Dyeing

6.1 Textile Coloration Using Plasma

Plasma treatment has been utilized for surface modification of cotton, ramie, wool, silk, and like fibers for improvement in their coloration. The improvement in the hydrophilic property (chemical changes) and increase in surface area/roughness (physical changes) were utilized in faster dye exhaustion and/or better K/S value, in addition to reduction in dyeing time and temperature. The DBD plasma treatment of cotton, wool, and polypropylene was found to change the hydrophobic character into hydrophilic. Specific surface area was found to increase significantly from 0.1 to 0.35 m^2/g in the cotton fabrics, resulting in increase in dye uptake [19]. Air and dichlorodifluoromethane (DCFM) plasma treatment on cotton fabrics led to improvement in dyeability with reactive and natural dyes. However, there was a small decrease in dyeability with direct dye [7]. With the use of dichloromethane with RF plasma (10 Pa) for 10–45 s on cotton and polyester fabrics, the dyeability with reactive dyes could be enhanced without affecting other properties [22]. Low-pressure plasma polymerization was carried out for 5–30 min on cotton fabric in amine ethylenediamine or triethylenetetramine (TETA) [43]. The treated fabrics were dyed with a reactive Remazol Black B dye. The maximum improvement in color value was 33.9 % compared to the untreated sample. This improvement in dyeing was due to the creation of chemical groups that were suitable for dye exhaustion and reaction. In the plasma-modified dyed samples, the rubbing fastness was very good for higher shade depths. Plasma treatment of cotton followed by TETA application could also be dyed with acid dyes with better color yield due to the formation of new amine groups as confirmed by FTIR analysis. Sun and Stylios in [66] reported an increase in reactive dyeing rate in the plasma-treated samples compared to the untreated cotton sample, which was visible after 40 min of dyeing time. The exhaustion of dye was possibly due to the formation of holes during O_2 plasma treatment that provided a new pathway of dye penetration. Dyeing of plasma pretreated cotton woven fabrics showed deeper and brighter shades [41]. Plasma treatment in the presence of air or oxygen increased both the rate of dyeing and direct dye uptake in the absence of electrolyte in the dye bath

(Chloramine Fast Red K) [65]. The oxygen plasma treatment was found to be more effective for textile coloration than the air plasma treatment. The increase in dye uptake in the cotton fabric was due to the cumulative effect of (i) the oxidative attack of cotton fiber that modifies the surface properties, (ii) change in fabric surface area per unit volume caused by surface erosion, (iii) the etching effect of fiber by plasma and removal of impurities such as wax, or any remaining size material, (iv) chemical changes in cotton fiber leading to the formation of carbonyl and carboxyl groups, and (v) the possibility of the formation of free radicals on the fiber surface [13]. When the nylon 6 fabrics were treated with cold plasma using nonpolymerizing gases, such as oxygen, argon, and tetrafluoromethane, improvement in dyeability with basic dyes was noticed due to etching of fiber and introduction of polar groups. When different monomer coatings were applied to polyester, polyamide, and polypropylene (PP) fabrics, it improved the affinity to other classes of dyes [68]. Low-temperature plasma treatment of grey, mercerized cotton and polyester/cotton blended fabrics before dyeing has been reported to be effective for improvement in dyeing. Silicon tetrachloride hydrophilic plasma coating on PET fabric was found to increase in surface roughness resulting in improvement of PET dyeing [34]. Plasma polymerization of acrylic-like coatings on polyester and polyamide fabrics was found to enhance wettability and dyeability with basic dyes and also improved soil-resistance properties [10]. The color depth of the dyed fabric (polyester/cotton blend) increased with the acrylic-like film thickness. The surface modification of PP fabrics by acrylonitrile cold plasma to deposit poly-acrylonitrile–like layers was reported to improve in water absorption and dyeing properties [59]. This was due to the presence of nitrogen- and carbon-based unsaturated linkages and the formation of secondary generation =C=O groups. Dyeing of polyamide fabrics was carried out after surface modification with DBD plasma (power –0.5–2.5 kW/min/m) [63], and it was found that the change from hydrophobic to hydrophilic was the key point for adsorption of aqueous dye solutions to achieve excellent dye uptake, a high rate of dyeing, good uniformity, and good fastness for darker shades using less concentration of dyestuffs at a lower time and temperature.

Protein fibers such as wool and silk were plasma treated in the presence of various gases and their effects on the rate of dye exhaustion, final dye uptake, K/S, and fixation have been reported by several research groups. Wool fiber was plasma treated using various nonpolymerizing gases to improve the hydrophilic properties in terms of water absorbency and surface roughness as discussed in Sect. 5.1. The improvement in water absorbency time might have enhanced the uptake of an anionic dye by 5 % at equilibrium compared to the control sample, when the dyeing was carried out at 70 °C. The improvement in dye uptake in the plasma-treated sample was mainly due to (i) partial destruction of the outer epicuticle layer of wool fiber, (ii) reduction of covalently bond fatty acid (18 methyl esacanoic acid) layer on the upper epicuticle, (iii) cystine (S–S) linkage reduced to cysteic acid (–SO_3H), and (iv) formation of an additional NH_2 group. XPS analysis showed that after 5 min N_2 plasma treatment, the carbon (C) percentage decreased by 8.5 % due to partial etching and removal of the long carbon hydrophobic fatty acid chain from the fiber surface. As expected, the N and O percentages in the treated samples increased by 16 and 39 %, respectively. It might be noted that the increase in N_2 percentage promotes the formation of additional NH_2 groups. The surface oxygen percentage increased due to surface oxidation and the same was confirmed by the reduction in sulphur (S) atomic percentage from 2.58 to 2.23 with a shift in sulphur atomic peak from 163 to 168 eV binding energy in the untreated to the plasma-treated samples, respectively [77]. Electrospin resonance (ESR) results showed the increase in the area under the curve by 18.2 times with G factor 2.007 in the plasma-treated sample due to the formation of more nitrogen-centered free radicals [38]. Similar results were also observed when the wool fabric was plasma treated in the presence of O_2 plasma. Two more physicochemical changes were observed, such as (i) additional formation of –C=O, –OH, and –COOH groups and (ii) a slight improvement in crystallinity. Plasma treatment enhanced the surface etching leading to an increase in surface area from 0.1 to 0.35 m^2/gm in the untreated to treated samples, respectively [19]. Sun and Stylios in [66] reported that plasma treatment could increase in scouring efficiency and dyeing rate by nearly 50 %. Improved dye uptake of the wool fabric as well as the depth of color irrespective of plasma gases used were reported by Ratnapandian et al. in [50]. In a similar study, wool fabric was treated for 5 min in O_2 plasma and dyed with acid, chrome, and reactive dyes at 50 °C with pH of 4.5. It was observed that in the case of acid, chrome, and reactive dyes, after 1 h of dyeing, the dye uptake increased by 72.6, 6.5, and 39.4 %, respectively. The result showed that the plasma treatment helped in faster dye exhaustion. However, after 2 h of dyeing at equilibrium, the total dye uptake increased by only 2 % compared to the untreated fabric for the acid- and the chrome-dyed fabric. On the other hand, 25 % more dye uptake was found for the reactive dyed sample at equilibrium. It might be possibly due to the formation of oxygen containing functional groups that could react with dye molecules. However, plasma etching and new dye site generation was not sufficient for the improvement of acid and chrome dyes at equilibrium [27]. According to Rombaldoni et al. [51], if O_2 plasma could be used for 5 min at 30 W for surface modification of wool followed by dyeing using a combination of 1:2 metal complex dyes at 98, 85, and 80 °C at a neutral pH, the final bath exhaustion of the plasma-treated sample could be comparable with the control sample dyed at 85 °C. The effect of atmospheric pressure on He plasma treatment for 6 min on wool fiber was studied using dichlorotriazine-based reactive dye (C.I. Reactive Red 2) at 35 °C by the pad batch method [44]. Plasma treatment resulted in significant improvement of color yield. Both the dye pick-up and the fixation of dye on wool fabric increased almost twice based on K/S values after plasma treatment of the samples. The liquid expression was found to increase by approximately 40–50 % in the plasma-treated sample resulting in high concentration of dye being applied on the fiber. Even after the removal of unfixed dye, the K/S values were found to increase by almost 100 % (1.5–2.5 for the untreated sample and 3.7–4.6 for the plasma-treated samples). The percentage of fixation was in the range of 80 ± 5 % for both the untreated and plasma-treated wool. The SIMS analysis showed an increase in the intensity of HO^- and NH^- groups, whereas the intensity of the CH^- peak decreased after the plasma treatment. This is an indication of formation of more numbers of $–NH_2$ groups resulting in better dye exhaustion and fixation.

Similar to wool, in Eri and Muga silk, the plasma treatment nearly doubled the wicking rate compared to the untreated silk [49]. After 30 min of low-pressure plasma treatment in the presence of O_2, N_2, and H_2 atmosphere, the coefficient of friction increased to 0.7–0.8 from 0.27 for the untreated sample. It was observed that after 10 and 30 min of O_2 plasma treatments, there was 13 and 22 % loss of crystallinity. Unlike hydrogen (H_2) plasma treatment, the O/C and N/C atomic ratios improved slightly in the O_2 and N_2 plasma treated samples. The effect of NH_3 plasma treatment on silk fabric has also been studied and found to improve the N atomic percentage considerably. However, improvement in reactive dye uptake was not so promising. Plasma treatment improved the dyeability and color strength of the silk fabric irrespective of gases used for treatment. Degummed silk fabrics were plasma treated in O_2, N_2, and H_2 atmospheres for 5 min and dyed with Ramazol reactive dye at 50 °C for 90 min. The K/S value of the treated fabrics improved significantly compared to the control fabric. The 5 min plasma-treated dyed fabric at 6 % shade exhibited the equal color strength of the 10 % dyed control sample. This might be because the plasma treatment helped in the formation of more active sites required for dyeing [21].

6.2 Textile Coloration Using UV

Wool is one of the important natural protein fibers and it has 1 % mass nonprotein material and 25–75 % impurities, such as grease, perspiration suint, dirt, and vegetable matter. Clean wool contains 82 % keratinous proteins with 18 different types of amino acids. Amino acids, such as glycine, alanine, phenyl alanine, valine, leucine, and isoleucine, are hydrophobic in nature, whereas serine, threonine, and tyrosine are hydrophilic in nature. The wool surface also has a hydrophobic characteristic due to the presence of a large number of disulphide cystine crosslinks in the exocuticle. Fatty acids are covalently bound to the protein by means of ester or thioester bonds. These chains are oriented away from the fiber to produce a polyethylene-like layer on the fiber surface, thus making the epicuticle hydrophobic. For this reason, wool exhibits a hydrophobic (water-repellent) characteristic even after the removal of wool grease by a scouring process or solvent extraction. Together, these act as a barrier against penetration of dye molecules and other chemicals in the fiber structure. Low-temperature plasma (LTP) has been explored for removal of this hydrophobic layer and improvement in dyeing properties as discussed above. UV pretreatment has also been used for similar surface modification and improvement in dyeing as discussed below.

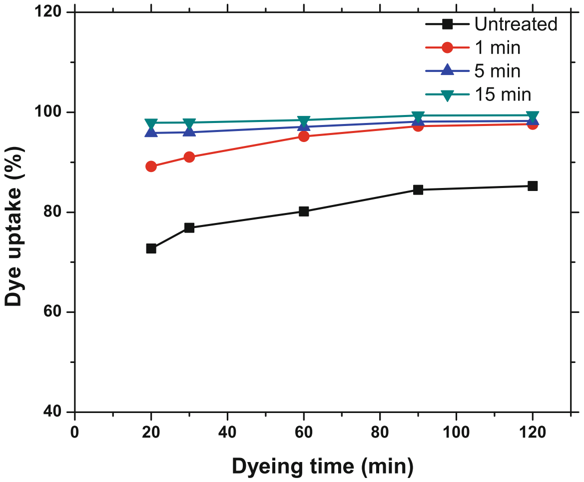


Fig. 5 Effect of UV irradiation time on dye uptake of wool fabric in N_2 atmosphere [3]

6.2.1 Dyeing with Acid Dye

Effect of Dyeing Time

Wool fabrics were dyed with acid dye (Navimill yellow 56 N) with 2 % shade keeping the dye bath at 60 °C, material-to-liquor ratio of 1:40, pH at 5. and acetic acid at 0.5 g/l [3]. The dye exhaustion was measured by sampling the dye bath concentration after 20, 30, 60, 90, and 120 min of dyeing. Absorbance of the dye solution was measured in UV-Vis spectrophotometer at 425 nm ($\lambda_{\text{max})}$. Figure 5 shows the dye exhaustion percentage corresponding to UV irradiation time for the different samples. It can be seen that the dye has a high affinity for wool as the exhaustion value in the untreated sample is quite high. However, after UV irradiation, the dye uptake (exhaustion) increased significantly. After 20 min of dyeing, the exhaustion percentage increased from 72.4 % in the untreated sample to 89.1 % in the 1 min UV-treated sample in nitrogen atmosphere with 16.7 % more dye uptake. With increasing UV irradiation time, the dye exhaustion percentage increased further to 97.9 % in the 15 min irradiated sample. In the untreated sample, dye uptake slowly increased with dyeing cycle time due to the availability of dye sites. In contrast in the UV-irradiated samples, the exhaustion percentage reached the maximum value within 20 min of dyeing cycle.

Further dyeing had happened at equilibrium condition except for the 1 min treated sample. It was interesting to observe that in the untreated sample, the dye uptake after 120 min of dyeing was 85.2 %, whereas the dye uptake was in the range of 89.1–97.9 % in 1, 5, and 15 min irradiated samples. This signifies that in the UV-irradiated samples, the dyeing cycle could be reduced by 100 min to achieve a similar uptake. This will help in saving a significant amount of energy in the textile coloration process.

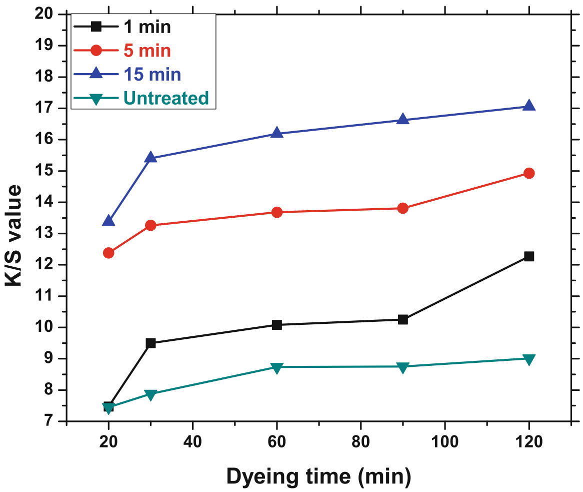


Fig. 6 Effect of UV irradiation time on K/S value of the wool fabric in N_2 atmosphere [5]

It can be seen from Fig. 6 that with increasing dyeing time, the K/S value increases, mainly due to the increase in dye uptake. It can also be seen that with increased UV irradiation time, K/S also increases. The 15 min–irradiated sample in the presence of N_2 atmosphere showed a darker shade compared to 5 and 1 min–treated samples [4]. This improvement in K/S value is mainly because of higher dye exhaustion in the fiber structure with increasing irradiation time. The increase in dye uptake was also attributed to the decrease in number of disulphide (S–S) linkages in keratin that act as an inhibiter for fiber welling and dye uptake. The other reasons for higher dye uptake are the destruction of the lipid surface barrier film and formation of more amine groups, in addition to an increase in surface roughness, which helps faster penetration of dye molecules. Upon UV exposure, degradation of cystine linkages leads to the formation of cysteic acid and some other intermediate products of cystine oxidation such as cystine monoxide and cystine dioxide were also formed. It provides a suitable site for introducing agents, such as dyes carrying a reactive group [33]. However, oxygen-rich groups might have been introduced at lipid carbon sites as well [9]. It was observed that in the 10 min UV-treated sample, the surface oxygen percentage increased to 27.5 from 10–12 % in the untreated sample. As discussed above, it might be due to the oxidation of disulphide sulphur (S–S) in the control sample to sulphonic acid (SO_3H). The untreated wool fabric showed major peaks at 285, 286.5, and 288 eV due to the presence of C–C/C–H bonds in the lipid layer; C–N, C–S, C–O groups and N=C=O of cystine groups, respectively. On the other hand, in the 9 min UV-treated wool fabric the unresolved peaks were observed at 287 and 289 eV due to the presence of the N–C–O group and carboxylic acid or ester group. These unresolved peaks are generated in the treated sample as a consequence of surface oxidation by high-energy UV photons [8, 74]. The increase in amine groups and different oxygen-containing polar groups, in addition to the removal of the

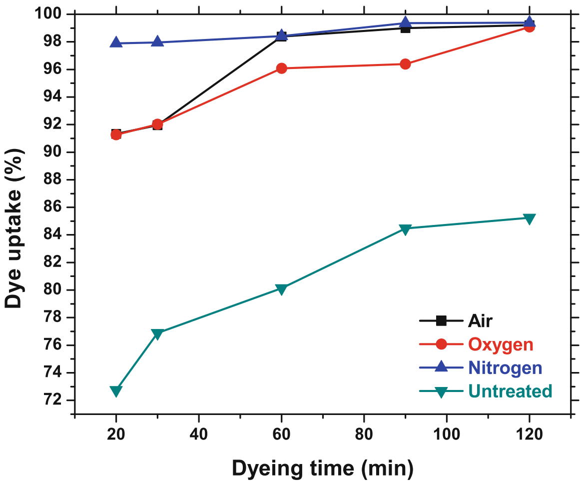


Fig. 7 Effect of different gaseous environments on dye exhaustion [4]

hydrophobic fatty acid layer and decrease in disulphide linkage cumulatively helped in rapid dye exhaustion even at a lower temperature. The wool fabric surface was modified using 253.7 nm UV irradiation for 40 and 60 min [74]. The XPS showed the sulphonate peak at 168.2–168.7 eV increased at the expense of the disulphide (S–S) peak at 163.6–164.0 eV upon UV irradiation due to surface oxidation of cystine. Dyeing of the samples was done at 45, 50, 55, and 60 °C using CI Acid Blue 7, and it was found that the dye uptake in the treated samples was always greater than the untreated sample. As discussed above, the reason for the increase in dye uptake was due to the decrease in the number of disulphides (S–S) in the keratin that acts as a crosslinking barrier near the fiber surface. The UV treatment could improve the dye uptake of CI Acid Blue 7 significantly by 30 and 15 % even at lower dyeing temperatures of 45 and 50 °C, respectively, and at short dyeing times of 30 min or less. The UV-treated and untreated samples had almost the identical adsorption isotherms as the number of free amino groups on wool remained unchanged, leaving the absorption properties unaffected. The diffusion coefficient of the UV-treated fibers was three times over the untreated fibers. The K/S value of the untreated fiber was 16.1 and it increased to 23.6 in the treated sample after 50 min of dyeing.

Effect of Atmosphere

Figure 7 shows the effect of different gaseous environments on exhaustion of dye in the untreated and the 15 min UV-irradiated wool samples [5]. It can be seen that in all the irradiated samples, the dye uptake was much more compared to the untreated samples. The dye uptake was only 72.7 % in the untreated sample and it increased to 91.3, 91.3, and 97.9 % in the air, O_2, and N_2 plasma-treated samples, respectively, after 20 min of dyeing. The sample treated in the N_2 environment showed a better result compared to the other gases. However, at the end of the dyeing cycle (after 120 min) all the irradiated samples showed a similar level of exhaustion. The improvement in dye uptake was highest in the N_2-irradiated sample and the lowest in the O_2-irradiated sample. The air-irradiated sample showed an intermediate result, as a major component of air is nitrogen only. When the samples were treated in the presence of oxygen and air atmosphere, the improvement in the K/S values were similar and were a little lower compared to the nitrogen-treated samples. This is because the dyeing of wool using acid dye depends on the number of amine groups present in the fiber structure. Possibly, the surface modification in nitrogen has helped in the formation of more amine groups that act as new dye sites. Similar findings have also been reported in other literature [70, 71].

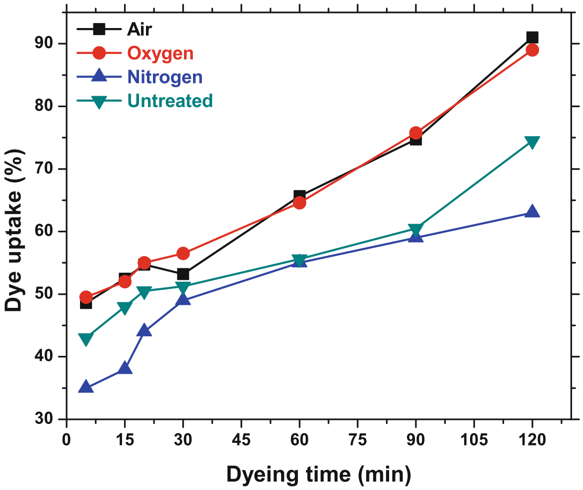
On the other hand, in the O_2-treated sample, the oxygen containing functional groups, such as C–O, C=O, O–C=O, and COOH were formed predominantly over amine groups, resulting in a lower dye uptake. Although these polar groups help in wetting and wicking, they do not have an active role in dyeing. Dye uptake represents the amount of dye taken up by the fibers from the solution, whereas diffusion represents the migration of dyes from the surface to the core of the fiber. The diffusion coefficient (DC) is related to the bulk property and was calculated using the Hills equation. It was found that the DC increased from 0.11 in the treated sample to 0.21–0.35 in the different plasma-treated samples. It was slightly higher in the O_2-treated sample than N_2 and air-treated samples. This may be due to a significant increase in the O/C atomic ratio after the UV treatment in O_2 atmosphere.

The SEM micrographs of the untreated sample showed a well-defined contour of scales and seem to have a smoother surface morphology. On the other hand, the treated fibers' surface appeared to be relatively less waxy irrespective of the gaseous environment used. Surface morphology of the treated samples in nitrogen atmosphere appeared to have a distinct feature compared to other irradiated samples. The typical scale geometry of wool was not visible and there were deep striations on the surface. Micropores were visible when the samples were exposed to O_2 atmosphere. Appearance of such surface features was due to the etching of the UV photon. These new features in the treated samples might have also helped in increasing surface area and a new pathway of dye molecule penetration.

6.2.2 Dyeing with Reactive Dye

The UV-irradiated samples were also dyed using reactive dyes in air atmosphere. It was observed that after UV irradiation, the K/S value significantly improved from 12.8 in the untreated sample to 25.8 in the treated sample. The effect of UV treatment in the different gaseous environments for Ramazol Black B reactive dye has also been reported [5]. The rate of dyeing or the dye uptake for the air, O_2, and N_2 treated wool fabrics were faster than that of the untreated sample. After 120 min of dyeing, the dye exhaustion was 85–89 % in the different UV-treated samples, whereas it was only 55 % in the untreated sample. As expected, with

Fig. 8 Dye uptake in the untreated and UV-irradiated samples in different atmospheres [3]



increasing dyeing time, the dye exhaustion was found to increase linearly. The UV treatment appears to cause etching associated with chemical modification and formation of C–O, C=O, O–C=O, C–O–O, and –OH groups that are responsible for enhanced dye uptake and dye–fiber interaction [36]. In a N_2 atmosphere, additional formation of $–NH_2$ groups also acted in favor of dyeing with anionic reactive dyes. It was observed that the loss in color strength upon washing was negligible in the both the untreated and treated samples. Excellent dye fixation was observed for all the treated samples (air, N_2, and O_2) and it was found satisfactory throughout the dyeing cycles. The additional dye taken by the fiber was covalently bonded to the protein molecule of wool rather than being deposited on the surface.

6.2.3 Dyeing with Basic Dye

The effect of UV irradiation in air, O_2, and N_2 atmosphere on wool fabric for 15 min on coloration using basic (cationic) dye (Methylene Blue) is plotted in Fig. 8. As expected, the dye exhaustion trend is different in comparison to dyeing with acid and reactive dyes. It can be seen that the rate of dye exhaustion and the total dye uptake by the irradiated samples in air and oxygen atmospheres were higher than the untreated sample. The sample treated in a N_2 atmosphere took less dye compared to the untreated sample. This implies that the exposure of the sample in nitrogen environment leads to formation of cationic amino groups that repel the positively charged basic dye molecules. Higher dye uptake in air- and O_2-treated samples was due to the formation of anionic groups that attracted the positive dye molecules.

The UV pretreatment for 10 min in air atmosphere followed by grafting with acrylic acid was found to improve the basic dye uptake in microdenier polyester fabrics [16]. The depth of shade on microfibers, otherwise very difficult to dye, increased with the irradiation time. The untreated sample was nearly colorless and the 10 min UV-treated and -dyed samples showed a deep blue shade (K/S = 11.51). The negative charge on the fiber surface attracts the positively charged dye molecules, which then get attached to the fiber by forming ionic bonds. Shade depth and K/S value were found to increase gradually with increasing UV irradiation time possibly due to the formation of free radicals on the fiber surface, etching of the fiber surface, and formation of more anionic polar –COOH groups. A similar study using UV excimer laser treatment on polyester microfibers followed by dyeing with disperse dyes (Dispersol Red DB and Dispersol C2R) has been reported [73]. Laser irradiation at 248 nm with 1 Hz repetition rate and laser facility of 70 mJ/cm^2 developed ripple-like structures and also enhanced the surface area. Initial faster dyeing rate and dye uptake in the treated samples (7 % more at equilibrium) indicated that the dye molecules could diffuse relatively faster and there was more availability of dye sites. The enhancement in surface areas upon laser treatment would have also facilitated swelling of the fiber that might have helped in better dye diffusion. Due to the surface physical changes, the treated samples gave lower spectral reflectance implying deeper dyeing.

7 Antistatic Finishing of Textiles

In the past, significant effort has been made to design suitable personal protective clothing to ensure workers' health, hygiene, and safety in hazardous work environments. In this regard, protection from static electricity is an important aspect, as it causes accidental ignition and fire in the paper, oil, gas, and plastic industries. The static charge buildup also adversely affects a garment's fall by clinging to the wearer's body and increases soil and lint pickup by the fabric. The term "static electricity" refers to the phenomena associated with accumulation of electrical charge in contact with and/or rubbing of the two objects. Synthetic fibers, such as polyester and nylon as well as natural fibers, such as wool do not have any conducting/wet layer on the fiber surface due to their hydrophobic character resulting in generation and accumulation of static charge. Many physical and chemical formulations for antistatic finishing of textiles have been developed, such as (i) grafting of the fiber surface, (ii) modifying the polymer (fiber) by copolymerization with a suitable monomer, (iii) use of metal particles and metal coatings on textiles, (iv) chemical finishes of fiber/fabric, and (v) and use of metallic fiber in the yarn or fabric structures [1, 12, 23]. These processes are water and energy intensive and cause environmental pollution. In contrast, cold plasma or UV eximer lamps can effectively be used for environmentally friendly antistatic finishing of textiles.

Table 3 Effect of plasma treatment on developed static charge and ½ decay time

Plasma treatment time (s)	Developed static charge (kV)		½ Decay time (s)	
	Air plasma	He plasma	Air plasma	He plasma
0	2.8	2.8	8.9	8.9
10	2.7	2.6	2.8	4.6
30	2.2	2.4	1.3	2.2
60	1.5	2.1	0.63	1.1

It was observed that after the plasma treatment both nylon and polyester fabrics became antistatic. The untreated nylon produced a 2.8 kV static charge and after 60 s the He plasma treatment sample produced only 2.1 kV static charge, that is, a 25 % reduction in static charge development as shown in Table 3. The static charge and half-decay (½) were measured using a STATIC HONESTMETER (Type H-0110-B, Shishido Electrostatic Ltd., Japan). In the air plasma-treated nylon samples, the reduction in development of the static charge was much more noticeable [56]. The 60 s air plasma-treated sample produced only 1.5 kV static charge, resulting in a 46 % reduction. It can be seen that with increasing plasma treatment time, the antistatic properties also improved. The antistatic performance of the samples could be measured by two methods, namely development of static charge and half-decay time. Half-decay time is the time that is required to dissipate half magnitude of the developed static charge. In the plasma-treated samples, the half-decay time (½ decay) decreased exponentially with plasma treatment time from 8.9 s in the untreated sample to 2.8 and 4.6 s in the 10 s air and He plasma-treated samples, respectively. After 60 s He-plasma treatment, ½ decay time was as low as 1.1 s, amounting to a reduction of ~88 % and in the air–plasma treated sample, it was lowest at 0.63 s, that is, a 93 % reduction. Polyester is more susceptible to charge buildup due to the absence of polar groups in the polymer backbone and low moisture regain (0.4 %). In such a sample, the developed static charge decreased from 1.53 kV in the untreated sample to 1.42 kV in the 60 s He–plasma treated sample. The half-decay time also was found to reduce significantly from 107 to 19.8 s in the untreated to plasma-treated samples, respectively. Air plasma could impart a better antistatic property compared to He–plasma. The improvement in antistatic property was due to the improvement in hydrophilic property, and increase in surface energy and surface area. The surface energy of the nylon fabric was found to increase from 49.5 to 63 mJ/m^2 in the untreated to plasma-treated samples, respectively. In polyester samples, it increased from 55 to >71 mJ/m^2. This happened due to the formation of various oxygen-containing hydrophilic groups as discussed in Sect. 5.1. It was also observed that in both plasma-treated nylon and polyester fabrics, there was formation of nanosized channels (SEM and AFM analysis). Due to the increase in the surface energy and the formation of nanosized channels, water spreading time decreased significantly as discussed in Sect. 5.1. AFM micrographs showed the plasma induced horizontal and vertical nanosized channels with dimensions of <100–200 nm. Due to the formation of such channel-like features in the treated samples, the surface area increased from 16.27 to 19.27 μm^2 in the nylon (18.3 % increase) and from 16.01 to 17.18 μm^2 in the polyester (7.3 % increase) compared to their respective untreated samples. The increase in surface area provided more area for charge dissipation resulting in lower ½ decay time (Table 3).

Low-temperature oxygen plasma (LTP) was employed on polyester fabric to improve the moisture content and the rate of static charge dissipation [32]. The effects of discharge power, treatment time, and system pressure were evaluated in this study. The optimum condition for improving the antistatic property was discharge power of 200 W, system pressure of 25 Pa, and 3 min of plasma treatment. The untreated polyester showed half-decay time of 1675.5 s and after plasma treatment it significantly reduced to 286 s, which is a bit more than commercially antistatic finished fabric (157.5 s). After plasma treatment, the moisture content of the sample improved to 5 % from 1 % in the untreated sample, whereas it was 1.41 % for the commercial finished sample. The SEM images showed the untreated sample had a smooth surface, and after plasma treatment, the surface became rougher (plasma etching) allowing moisture capture from air. The improvement in moisture content and antistatic property were associated with an increase in O/C ratio from 0.29 in the untreated sample to 0.58 in the plasma-treated sample due to the generation of –OH and –COOH species. In a similar study, it was observed that with increasing plasma discharge power, the half-life decay time decreased linearly [28]. In higher plasma discharge power, the ions and active species of plasma interact actively with textiles, resulting in better antistatic, physical, and chemical properties. With decreasing plasma pressure and treatment time, the half-life decay time increased, thus adversely affecting the antistatic property due to the smaller amount of interactions between the plasma species and textile. Similarly, plasma treatment of O_2, N_2, and a mixture of hydrogen–nitrogen (25 % H and 75 % N_2) on wool was carried out to impart an antistatic property [31]. The samples were treated in low-pressure glow plasma for 5 min and it was found that surface resistivity decreased from $263.25 \times 10^{11}\ \Omega$ to $182.5 \times 10^{11}\ \Omega$ in the untreated to H–N_2 plasma-treated samples (warp direction). It was also noticed that on plasma treatment, the resistance decreased in the following order: untreated > nitrogen–plasma-treated > oxygen–plasma-treated > H–N_2 plasma-treated samples. Similar results were also observed for both in the warp and weft directions of the fabric. Plasma etching makes the wool surface hydrophilic, decreases the crosslinking on surface layers, and increases the sorption behavior of wool by enhancing the hydrogen bond forming capacity between the fiber and water molecules. Thus, water on the fiber surface forms a continuous film allowing free movement of ions resulting in an increase in conductivity and decrease in discharge time. Upon plasma treatment, the wetting time was found to reduce from 900 s in the untreated sample to less than 1 s in the plasma-treated sample. The breaking load was found to increase marginally in the plasma-treated samples due to increases in interyarn and interfiber friction.

8 Hydrophobic Finishing of Textiles

Hydrophobic textiles are important in many applications, because liquids are abundant in the form of rainwater, food, beverages, chemicals, and pesticides. Unavoidable interaction of these liquids with textiles causes unwanted wetting, staining, or contamination. Hydrophobic textiles help to protect textiles as well as their users from staining or enabling the liquid droplets to roll off leaving the underlying materials unchanged. There are three important aspects in hydrophobic finishing of textiles (i) surface energy of the base materials, (ii) surface energy of the coated materials, and (iii) surface energy of the liquid. All the solid surfaces have a distinct surface energy, which is a function of surface area and the molecules that are present on the surface. Similarly each liquid has a specific surface tension, which is a measure of interaction energies between the liquid molecules. In hydrophobic finishing of textiles, the surface energy of the base materials is reduced by coating or grafting with a material of low surface energy. Mainly hydrocarbon-, fluorocarbon-, and silicone-based compounds are used for such modification. Hydrocarbon and silicone help in producing water-repellent hydrophobic textiles. On the other hand, fluorocarbon chemicals are used for oil-repellent finishing of textiles in addition to water repellency. Hydrophobic finishing of textiles using plasma is carried out by plasma polymerization, plasma coating, or plasma deposition of silicone, hydrocarbon, or fluorocarbon liquid or gaseous precursor. Glow plasma was generated at an atmospheric pressure in the mixture of 1,3-butadiene (hydrocarbon monomer) and He gas for hydrophobic finishing of cellulosic textiles [57]. After 1.5 min of plasma reaction, the water absorbency time was found to significantly increase to 28.5 min from <1 s in the untreated sample. With increasing plasma treatment time, water absorbency time increased to $>3{,}600$ s in the 12 min plasma-treated sample. In this sample, the water contact angle increased to 142 from $\sim 0°$ in the untreated sample. The hydrophobic finish was found to be durable to soap washing. In the untreated sample, the carbon atomic percentage was 57.1 % and it increased to 85.2 and 90.9 % in 1.5 and 12 min plasma-treated and soap-washed samples, respectively. A similar reduction in oxygen percentage was observed due to the depletion of $-$OH bond of cellulose. The increase in carbon percentage helped in formation of $-CH_x$ containing hydrophobic species, such as $-CH$, $-CH_2$, and $-CH_3$. SIMS analysis showed a similar result, where the ratio of total hydrophilic molecules to total hydrophobic molecules reduced from 1.87 in the untreated sample to 0.64 in the 12 min plasma-treated sample. GC-MS analysis revealed that mainly two types of species were formed: based on a dimer of 1, 3 butadiene (110 and 108 amu) and species with seven carbon atoms (96 amu). Based on the XPS, SIMS, GC-MS, and other analysis, a possible mechanism of plasma reaction of 1, 3-butadiene with cellulose has been reported. After the plasma reaction, the individual fibers in the yarn structure were visible and there was no blockage of interfiber spacing observed under SEM. This had happened possibly due to the nanoscale surface modification of fibers.

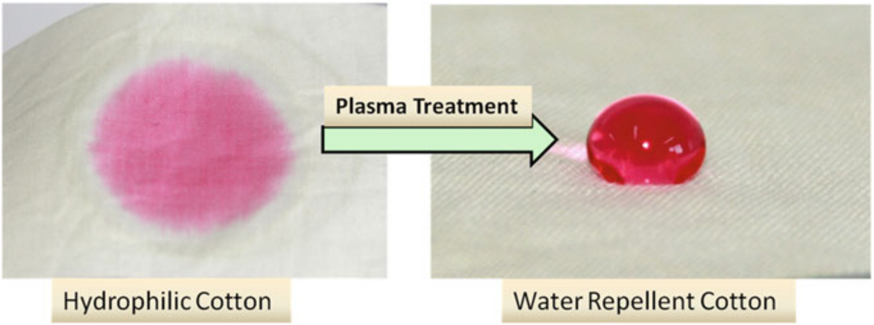


Fig. 9 Conversion of hydrophilic cotton into hydrophobic by plasma reaction [58]

Atmospheric pressure helium–fluorocarbon (He/FC) cold plasma has been used to impart a high degree of hydrophobic functionality in cotton textiles [58]. After the plasma reaction for 3–8 min, it was observed that hydrophilic cotton turned into a highly hydrophobic one. As a result of this, a water droplet was not absorbed by the fabric even after 1,800 s, whereas in the untreated sample it was absorbed within 4 s as shown in Fig. 9. The water contact angle in the plasma-treated sample was as high as 140° compared to ~0° in the untreated sample. FTIR analysis of the treated sample showed the presence of different fluorocarbon species and EDX analysis showed ~4 % fluorine atoms present on the fabric surface, which were responsible for the development of hydrophobicity in the otherwise hydrophilic cotton. Similar finishing of textiles by the traditional wet chemical process requires ~10 L of water and takes 20–30 min time, besides being energy intensive. On the other hand, plasma processing of textiles, being a water-free dry process, can save a large quantity of water and energy. Vinogradov ans Lunk in [69] studied the deposition of the fluorocarbon layer on the surface of Si wafers and technical textiles in the presence of DBD plasma using CF_4, C_2F_6, C_3HF_7, $C_2H_2F_4$, C_3F_8, and C_4F_8 fluorocarbon molecules. It was found that fluorocarbon polymer films can be deposited, if the ratio of F/C atoms in the starting fluorocarbon molecules is smaller than three (3). The deposition of the fluorocarbon layer was confirmed using FTIR and XPS analysis. The effect of CF_4 and C_3F_6 plasmas on the surface properties of cotton fabric was studied by McCord et al. in [37]. The hydrophobic functionality was reported to increase after treatment with both the plasma gases. XPS analysis showed an increase in surface fluorine content to ~1–2 and 2.3–7.8 %, respectively, in CF_4 and C_3F_6 plasma-treated cotton fabrics. Based on the XPS analysis, the possible mechanism of plasma reaction with cellulose has been proposed. The effect of SF_6 plasma treatment on the hydrophobic property of silk fabric was reported by Kamlangkla et al. in [26]. The improvement in the hydrophobic property was attributed to the attachment of –CF, $–CF_2$, and $–CF_3$ molecules to silk fabric, and it also depended on the pressure of the plasma reactor and power.

9 Hydrophobic/Hydrophilic Finishing of Textile

Multifunctional wool and silk fabrics having the hydrophobic property on one side and the hydrophilic property on the other side is an interesting area of research in the development of smart textiles. This kind of special fabric, that is, with both hydrophilic and hydrophobic functionalities in one fabric has not been produced by plasma treatment thus far. Periyasami et al. in [47] functionalized one side of mulberry silk fabric by 172 nm UV excimer lamp. It has been elucidated that after one side irradiation for 5 min in air atmosphere, wetting and wicking properties could be improved significantly on the irradiated side. The UV irradiation showed an average wetting time of 7.2 s, which was 60 % lower than the control silk fabric. However, the other side, that is, the nonirradiated side of the fabric showed behavior similar to the control silk. In the treated surface, the wetting/wicking of water was better due to the improvement in the hydrophilic property in addition to formation of nanopores of 100 nm × 10 nm, and the surface morphology of the other side (not treated) remaining unchanged. Later on based on this concept, in 2012 Basak et al. in [4] developed hydrophilic–hydrophobic wool fabric by 172 nm UV excimer lamp. Scoured wool fabric was initially treated with a fluorocarbon chemical to make the sample hydrophobic (both sides). Then one side of the hydrophobic sample was exposed to UV irradiation for 5–30 min. It was found that with increasing UV irradiation time, hydrophilic properties in terms of wetting, wicking, and contact angle improved significantly. The contact angle of the scoured wool (control sample) was 90° and it increased to 140° in the fluorocarbon-treated sample. It was seen that the contact angle on the irradiated side of the fabric decreased exponentially with increasing irradiation time. The contact angle decreased to 60° within 5 min of UV exposure and it was as low as 10° after 30 min of irradiation. The other side of the fabric, that is, the unexposed side remained completely hydrophobic (water-repellent) and there was no visible change in contact angle. It might be because the high-energy UV irradiation (7.2 eV) on the fluorocarbon finished fabric caused photo-induced oxidation involving defluorination of the surface and incorporation of oxygen by forming $CF{-}O{-}CF_2$, $CF_2{-}O{-}CF_2$, and $CF{-}O{-}CF_3$ moieties [29, 48].

10 Antifelting Finishing of Wool

Wool fabric is felted in an aqueous medium by mechanical agitation due to the presence of scale on the fiber surface. The bombardment of high-energy plasma species on wool has been explored for antifelting finishing. It has been reported that plasma treatment damaged the scales and oxidized the upper fatty layer to produce shrinkproof wool [19]. The untreated wool fabric showed 12.3 % shrinkage compared to only 2 % shrinkage in the plasma-treated wool [30]. The SEM micrograph showed that the O_2 plasma treatment could etch the fiber surface and break the part of the surface scales that helped in imparting antifelting characteristic. For further improvement in shrink resistance properties, the plasma-pretreated sample was treated with 5 % aminofunctional poly-dimethyl siloxane. It showed excellent antifelting properties with almost no change in the fabric handling [40]. Recently, plasma-pretreated wool has been grafted with chitosan polymer and significant improvement in the antifelting property has been demonstrated [61].

In Dood et al. [11] reported that UV treatment is also effective for shrinkproofing of wool fabric treated with silicone polymer. In this process, UV treatment helps to achieve adequate shrinkproofing (only 3 % shrinkage) of wool fabric treated with only 3 % silicone-containing polymer compared to the 20 % shrinkage of untreated wool fabric. UV treatment helps to adhere silicone polymer on the wool surface better so that it can maintain its shrink-resistance properties even after washing cycles. There was only a marginal change in tensile strength and weight loss properties. Sayed and Khatib in [60] reported that the UV treatment can modify wool fabric to enhance its felting shrinkage and pilling resistance properties. In this study, freshly scoured wool fabric was first irradiated with 254 nm UVC radiation for 10 to 60 min followed by treatment with an eco-friendly oxidizing agent such as H_2O_2 or proteolytic enzyme. It was found that UV/H_2O_2-treated wool fabric showed lower area shrinkage of 13.7 % compared to 32.6 % in the control wool fabric. Shrinkage and pilling resistance results of the treated fabric were compared with harsh and non-eco-friendly chlorination treatment. The results were attributed to the fact that UVC radiation could partially oxidize wool fiber surface (–S–S into $-SO_3H$), oxidize the thin fatty lipid layer of the upper epicuticular, and break the waxy smooth scales responsible for felting. These physicochemical surface changes facilitate the adhesion and penetration of H_2O_2 inside the modified wool fabric. Treatment of wool fabric with these systems was found to be effective in reducing pilling and shrinkage without severe loss in weight and strength of the fabric.

11 Conclusion

The chemical processing of textiles is important, as it imparts the highest value to the textile. However, during wet chemical processing of textiles, the industry causes significant water and air pollution in operations such as padding, drying, curing, and postwashing. The cost of the final product also increases due to the multiple numbers of drying operations and effluent treatment. There is a need to have two approaches to address these issues: reduce the consumption of water in wet chemical processing either partially or fully, and modify the surface of the fibers or the fabric to reduce consumption of chemicals and energy. Among the various techniques of surface modification, plasma and UV treatment are the most promising emerging technologies for engineering of fiber surfaces at a nanometer level, while avoiding the usage of water. Only low-temperature (cold) plasma either at atmospheric pressure or at low pressure is suitable for treatment of heat-sensitive textile substrates. Similarly, high-energy UV photons (7.2 eV) with wavelength <200 nm are mostly used for textile modification. Plasma and UV treatment of textiles using nonpolymerizing gases (small molecule), such as oxygen (O_2), nitrogen (N_2), air, argon (Ar), helium (He), and the like, brought both physical and chemical changes to the substrates due to surface cleaning, activation, oxidation, etching, radical formation, polymerization, and creation of nanostructures.

Due to the chemical changes, there was an increase in surface oxygen and nitrogen percentage. This leads to formation of the amine group (silk, wool, nylon), –COOH and C=O groups (polyester, wool, cotton), –OH (wool, cotton), sulphonic acid ($-SO_3H$) group (wool), and the carbonyl group (cotton). Similarly, due to the physical changes there was a formation of vertical channels with dimensions of <200 nm (nylon), horizontal channel with size of 100 nm (polyester), nanopores of 100 nm × 10 nm (silk), and microcrack (cotton). The above physical and chemical changes result in significant improvement in water absorbency time, wetting time, wicking time, oil absorbency time, and surface energy. It is interesting to observe that in nylon fabric, oil spreading time decreases from 152 s in the untreated sample to 52 s in the 60 s He–plasma-treated sample. In the plasma-treated samples, there was an increase in surface area from 16.27 to 19.27 μm^2 (nylon), from 16.01 to 17.18 μm^2 (polyester) and from 0.1 to 0.35 m^2/gm (wool) in the untreated to plasma-treated samples, respectively. This increase in surface area in addition to the chemical changes helped the textile to produce not only less static charge, but also to dissipate the same at a faster rate. The 60 s air–plasma-treated sample produced only a 1.5 kV static charge compared to 2.8 kV in the untreated sample. Similarly, the half-decay time was found to reduce sharply from 8.9 s in the untreated sample to 0.63 s in the 60 s air–plasma-treated sample.

Chemical changes play a more active role in the improvement of dyeing of plasma- and UV-treated wool, silk, cotton, and polyester fabrics than the physical changes. In wool fiber, in addition to formation of amine groups, removal and/or oxidation of the fatty hydrophobic layer on the epicuticle, and reduction in the disulphide cystine linkage helps in better dye exhaustion. Removal or partial damage of scale upon plasma and UV irradiation leads to the development of antifelting woolen textiles. Cotton and silk can made hydrophobic without using water by plasma reaction of hydrophobic precursor (butadiene) and fluorocarbon precursors (CF_4, C_2F_6, C_3HF_7, $C_2H_2F_4$, C_3F_8, $C-C_4F_8$, and SF_6). Specialty wool and silk textiles, such as one side being hydrophilic and other side hydrophobic can be produced by UV excimer treatment. The treated fabric surface is hydrophilic in nature with a water contact angle of 10° compared to the untreated surface with a contact angle of 140°, which is highly hydrophobic. Plasma- and UV-induced surface modification of textiles occur at the nanometer level, hence the bulk physical and chemical properties remain unaltered. As, these processes are carried out in a dry state, adoption of such emerging technologies will help to develop superior product quality in textiles at a lower cost, while addressing the negative environmental issues.

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Sustainable Textile Wet Processing: Applications of Enzymes

A. K. Roy Choudhury

Abstract Enzymes are a sustainable alternative to the harsh toxic chemicals in the textile industry. As enzymes operate in moderate conditions of temperature and pH, energy consumption is reduced, thereby reducing greenhouse gas emissions. Both water consumption and waste generation during textile manufacturing are also minimized by enzyme use. As the enzymes are very specific in their actions, minimum by-products are generated. The risks to humans, wildlife, and the environment are minimized. Enzymes can be utilized in several steps of textile processing namely desizing, scouring, bleaching, and biopolishing of cotton, degumming of silk, bleaching and shrinkproofing of wool, biostoning (of denim), and for treatment of textile effluents.

Keywords Enzymes · Green chemistry · Desizing · Scouring and bleaching · Biopolishing · Biostoning · Aerobic and anaerobic treatments

1 Introduction

One major area of application of biotechnology is the use of proteins called enzymes which are composed of amino acids. Enzymes are large biological molecules responsible for thousands of metabolic processes that sustain life. The global market for industrial enzymes increased from US$ 1.5 billion in 2000 to US$ 2.25 billion in 2007. Approximately 10 % of industrial enzymes find their application in textile processing [89]. In textile pretreatment of natural fibers, such as depilling, desizing, scouring, and so on, enzyme technology has already proven to be very profitable. The impact of biotechnology in the textile industry is mainly

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at three levels: the use of enzymes in wet preparatory processes and laundry detergents, in the design of new and biodegradable fibers, and in the treatment of textile effluent.

Biocatalysis is a tool of increasing importance for industries that aim at sustainable development. Biocatalysis has been known to human beings from ancient times: the description of various beer recipes was found in Sumerian writing. In the nineteenth century Louis Pasteur concluded that the fermentation of sugar to alcohol by yeast was catalyzed by a vital force contained within yeast cells called "ferments", which were thought to function only within living organisms. Wilhelm Kühne was first to use the term "enzyme" and years later Emil Fisher proposed the "lock and key model" to visualize substrate and enzyme interaction [56]. Enzymes are produced by all living organisms in the fermentation industry by moulds or bacteria, but they themselves are not living organisms.

The enzymatic desizing of cotton with α-amylases has been in vogue for many decades. Various other enzymes are also being used in different cotton pretreatment and finishing processes [57]. The enzymes are also being used on other natural fibers. Examples are the enzymatic degumming of silk with sericinases [33], the feltfree-finishing of wool with proteases [27], or the softening of jute with cellulases and xylanases [47]. The surface treatment of synthetic fibers such as polyester [102] or polyacrylonitrile [92] with enzymes have been studied extensively.

To date more than 3,000 different enzymes have been isolated and classified. However, only a limited number of enzymes are commercially available and an even smaller number are used in large quantities. More than 75 % of industrial enzymes are hydrolytic in action. Protein-degrading enzymes constitute about 40 % of all enzyme sales. Detergents (37 %), textiles (12 %), starch (11 %), baking (8 %), and animal feed (6 %) are the main industries that use about 75 % of industrially produced enzymes [86]. Major companies involved in the preparation and marketing of enzymes are Novozymes (formerly Novo Nordisk), Genencor, DSM, Röhm and Haas, and Clariant (formerly Sandoz), among others.

The enzymes differ from each other due to the following features:

- Differences in amino acids present
- Difference in the sequence of amino acids in the structure
- The presence or absence of metal ions
- The structure conformation as a whole.

Recent studies [14] show that biotechnology in the textile industry reduces water usage and energy demand for bleaching (biocleanup) by about 9–14 and 17–18 %, respectively, or could cut water consumption by as much as 30–50 % (bioscouring) and costs associated with water usage and air emission by about 50–60 % (biostone washing) in China. Evidently, the application of textile biotechnology can result in cleaner processes that produce less waste and use less energy and water. Enzymes are one of the most promising approaches to pollution prevention, resource conservation, and cost reduction.

2 Enzymes

Enzymes are biological catalysts. The term "enzyme" was first used by Kühne in 1878 and is derived from the Greek word *enzumé* meaning "in (*en*) yeast (*zumé*). Chemically enzymes are proteins of high molecular weight: for example, that of enzyme α-amylase of *Bacillus subtilis* is about 100,000. They consist of complex three-dimensional proteins composed of polypeptide chains. They range from individual proteins with a relative molecular mass (RMM) of around 13,000 catalyzing a single reaction, to multienzyme complexes of RMM of several millions catalyzing several distinct reactions. Additionally some enzymes require some specific small nonprotein molecules, known as cofactors, in order to function as catalysts. Enzymes are relatively fragile substances and they are susceptible to denaturing, that is, degradation due to temperature, ionizing radiation, light, acids, alkalis, and biological factors and thereby become inactive.

Commercially enzymes are obtained from three primary sources: animal tissue, plants, and microbes. Natural enzymes are not readily available in sufficient quantities for industrial use. They are largely manufactured by fermentation, the technique well known for more than 3000 years. Microorganisms producing enzymes important for the textile industry are listed in Table 1 [83].

2.1 *Merits/Demerits of Enzymes*

The advantages of using enzymes are as follows [13]:

- The rate of a reaction is accelerated by lowering the activation energy of reaction. The enzyme remains intact at the end of reaction by acting as catalyst.
- Remarkable chemical precision due to far greater reaction specificity even in the absence of functional group protection. Enzyme engineering can further improve their stability and specific activity.
- Processes are easy to control as the enzyme activity depends upon operating conditions.
- Enzymes are biodegradable and eco-friendly.
- Applicable under milder conditions of temperature (below 100 °C), pressure (atmospheric), and pH (around neutral). However, high-temperature–stable enzymes are also available nowadays for faster reactions.
- Lower energy input leading to lower cost and lower emission of greenhouse gases to the environment.
- Enzymatic reactions are several orders of magnitude faster.
- Rarely are by-products generated.
- Fewer wastes are generated, thereby disposal problems are minimized.
- Safe to handle and noncorrosive.
- Reduced pollution loads due to easy biodegradability of enzymes.

Table 1 Microorganisms and the corresponding enzymes produced

Microorganisms	Enzymes produced
Bacteria	
Bacillus subtilis	Amylase
B. coagulans	α amylase
B.licheniformis	α amylase, protease
Fungi	
A. niger	Amylases, protease, pectinase, glucose oxidase
A. oryzae	Amylases, lipase, protease
Candela lipolytica	Lipase
P. notatum	Glucose oxidase
Rhizopus sp	Lipase
Trichoderma reesei	Cellulase
T. viride	Cellulase
Ascomycetes	α amylase
Basidiomycetes	α-amylase
Aspergillus sp	Pectinaseù lipase

- Safely dischargeable after use, sometimes after inactivation by changing pH or temperature.
- Reduction in global warming, saving in acidification, and nutrient enrichment [60].

Some of the problems and challenges of enzyme application are [50]:

- Enzyme recovery and reuse.
- Scale-up in industrial environment.
- Higher process time.
- May not always be economically feasible.

Precautions to be strictly followed are:

- Live steam should not be used.
- Chemicals should be added in prediluted form.
- Compatible ionic surfactants should be used.
- Nonionic wetting agents with appropriate cloud points are preferred [76].
- The temperature, pH, and heavy metal contamination should be closely monitored.
- The enzymes should be carefully stored under prescribed conditions.

2.2 *Enzyme Classification*

The International Commission of Enzymes (EC) established in 1956 by the International Union of Biochemistry (IUB) in consultation with the International Union of Pure and Applied Chemistry (IUPAC) wanted to classify hundreds of

Table 2 Six types of enzyme-catalyzed reactions

Class	Name of enzyme	Type of reactions
EC 1	Oxidoreductases	Catalyze oxidation/reduction reactions
EC 2	Transferases	Transfer a functional group (e.g., a methyl or phosphate group)
EC 3	Hydrolases	Catalyze the hydrolysis of various bonds
EC 4	Lyases	Cleave various bonds by means other than hydrolysis and oxidation
EC 5	Isomerases	Catalyze isomerization changes within a single molecule
EC 6	Ligases	Join two molecules with covalent bonds usually at the expense of an energy source (usually ATP)

enzymes available on the market and developed a nomenclature for enzymes, the EC numbers; each enzyme is described by a sequence of four numbers preceded by "EC". The first number broadly classifies the enzyme based on its mechanism of action.

The enzymes can be classified into six broad groups (top-level classification) according to the type of catalyzed reactions as shown in Table 2.

The nomenclature of an enzyme may be EC 4.2.1.20 which indicates that the enzyme belongs to the 4th main class, 2nd subclass, and 1st sub-subclass having serial number of 20. The complete nomenclature can be browsed at http://www.chem.qmul.ac.uk/iubmb/enzyme/.

2.3 Enzyme Action

Enzymes work mostly on renewable materials. Fruit, cereals, milk, fats, cotton, leather, and wood are some typical candidates for enzymatic conversion in industry. However, their use is not limited to natural materials. Quite recently it has been demonstrated that enzymes are able to modify the surfaces of synthetic textile materials such as polyester and polyamide.

Most enzymes are much larger than the substrates they act on, and only a small portion of the enzyme (around 2–4 amino acids) is directly involved in catalysis. The region called the "active site" contains these catalytic residues. The substrate is bound at the active site and then the reaction proceeds. Enzymes can also contain sites that bind cofactors, which are needed for catalysis. As are all proteins, enzymes are long linear chains of amino acids that fold to produce a three-dimensional product. Each unique amino acid sequence produces a specific structure, which has unique properties. Individual protein chains may sometimes group together to form a protein complex. Most enzymes can be denatured—that is, unfolded and inactivated—by heating or chemical denaturants, which disrupt the three-dimensional structure of the protein. Depending on the enzyme, denaturation may be reversible or irreversible.

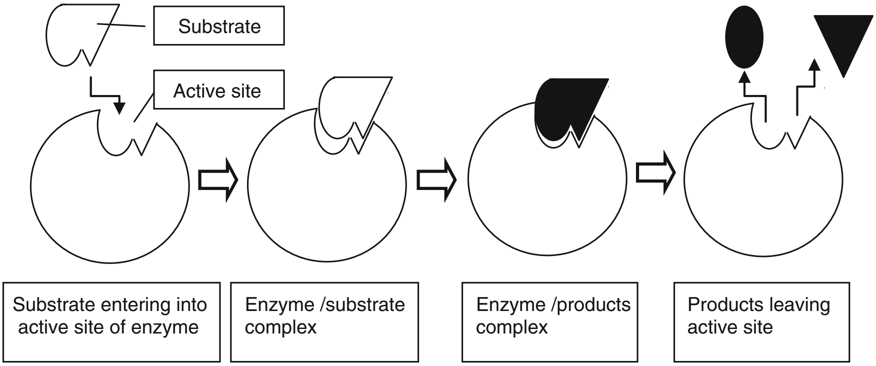

Fig. 1 Lock and key model of enzyme action

Enzymes are very specific in action. Nobel laureate organic chemist [25] suggested the simplistic “lock and key” model. Both the enzyme and the substrate possess specific complementary geometric shapes that fit exactly into one another. The high substrate specificity of enzymes is due to the individual architecture of the active site where only certain molecules can “stereo-fit in”. The enzymes have a true activity center in the form of fissures, holes, pockets, cavities, or hollows. The active site is a perfect fit for a specific substrate and once the substrate binds to the enzyme no further modification is necessary. The enzyme catalysis operates first to form an enzyme–substrate complex as shown in Fig. 1. At the active site on the enzyme, hydrolysis of the substrate is accelerated. The decomposition products of the substrate thus formed are usually unstable in the active site due to steric hindrances that force them to be released and return the enzyme to its initial unbound state so that further substrate is reabsorbed on the active site of the enzyme. The process continues until the enzyme is deactivated by conditions in the processing bath. Deactivation may occur by competitive or noncompetitive chemicals called “bogies” in the processing bath. The competitive bogies compete with the substrate for enzyme, whereas noncompetitive bogies are adsorbed on the enzyme causing the shape of the enzyme to change; both prevent enzymatic catalysis from occurring. All enzymatic systems function best within a narrow range of pH and temperature; too far outside the range, the enzyme becomes deactivated by changes in the three-dimensional structure. As the enzyme twists and coils into a shape that prevents sorption between enzyme and substrate, catalysis no longer occurs.

However, although this model explains enzyme specificity, it fails to explain the stabilization of the transition state that enzymes achieve. Daniel Koshland [45] suggested a modification to the lock and key model called the “induced fit model”: the substrate induces a change in the shape of the active site to the correct fit. Because enzymes have rather flexible structures, the active site is continually reshaped by interactions with the substrate [94]. As a result, the substrate does not simply bind to a rigid active site; the amino acid sidechains that make up the active site are molded into the precise positions that enable the enzyme to perform its catalytic function.

In some cases, as in the case of glycosidases, the substrate molecule also changes shape slightly as it enters the active site. The active site continues to change until the substrate is completely bound, at which point the final shape and charge are determined [9].

Most of the enzymes are inactivated or destroyed by temperatures over 75 °C. Once destroyed, they cannot be revived or reactivated. Currently thermostable enzymes (such as α-Bacillus subtilis, α-Bacillus licheniformis, etc.) are available that can withstand temperatures up to 90 °C. Certain enzymes require some specific bivalent metallic ions (e.g., Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, etc.) as activators which probably act by stabilizing the enzyme–substrate complex or sensitizing the substrate to the attack of enzymes. Certain chemicals such as alkalis, antiseptics, and acid-liberating agents tend to inhibit enzyme activity.

2.4 Blue Enzymes for Green Chemistry

Green Chemistry, the term coined by Paul Anastas in 1991 [3], is the design of sustainable chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

Among the different existing oxidant enzymes, laccases (benzenediol: oxygen oxidoreductases; EC 1.10.3.2) have been the subject of intensive research in the last decades due to their low substrate specificity [17]. Laccases are a group of oxidative enzymes whose exploitation as biocatalysts in organic synthesis has been neglected in the past, probably because they were not commercially available. The use of laccases in the textile industry is growing very fast, because in addition to to decolorizing textile effluents, laccases are used to bleach textiles [95], to modify the surface of fabrics [106], and to synthesize dyes [81]. Therefore, laccase-based processes might replace traditional high chemical, energy, and water-consuming textile operations. The enzyme can be applied at a temperature range of 30–50 °C at a pH of 3–5.

Laccases (EC 1.10.3.2, p-diphenol: dioxygen oxidoreductase) belong to the so-called blue-copper family of oxidases [6]. Laccases are multi-copper oxidases expressed under ligninolytic conditions by white-rot fungi. They are glycoproteins, which are ever-present in nature; they have been reported in higher plants and virtually every fungus that has been examined for them [8].

Laccases have relatively lower redox potential (450–800 mV) compared to those of ligninolytic peroxidases (>1 V), so it was initially thought that laccases would only be able to oxidize phenolic substrates [44]. However, the range of substrates oxidized by laccases can be increased through a mediator-involved reaction mechanism. *Mediators* are low-molecular–weight compounds that are easily oxidized by laccases producing, in some cases, very unstable and reactive cationic radicals, which can oxidize more complex substrates before returning to their original state. The electrons taken by laccases are finally transferred back to oxygen to form water [99]. In view of the low redox potential, native laccases can oxidize only phenolic fragments of lignin, with the concomitant reduction of O_2. However, the oxidation of nonphenolic substrates can also take place on mediation by appropriate substances. One such mediator is 2,2′,6,6′-tetramethylpiperidine-*N*-oxyl (TEMPO) [24].

The laccase mediator system (LMS) has yet to be applied on a large scale due to the high cost of mediators and the lack of studies that guarantee the absence of toxic effects of these compounds or their derivatives. The use of naturally occurring laccase mediators would present environmental and economic advantages.

At present, the main technological applications of laccases are in the textile, dye, or printing industries—in processes related to decolorization of dyes [52]—and in the pulp and paper industries for the delignification of woody fibers, particularly during the bleaching process [30]. In most of these applications, laccases are used together with a chemical mediator.

It is known that white-rot fungi are able to perform lignin degradation using a cocktail of oxidative enzymes, including laccases, despite the fact that the bulkiness of this polymer prevents direct interaction with these enzymes. Indeed, it has been shown that the treatment of pulp with laccase alone does not catalyze the degradation of lignin but instead leads to only minor structural changes and depolymerization [71]. To explain this puzzling situation, it has been hypothesized that small molecules might act as redox shuttles between the enzyme active site and the lignin core and cause polymer debranching and degradation [28]. Nowadays, this is regarded as more than just a hypothesis because the effect of chemical mediators, such as 3-hydroxyanthranilic acid, on laccase-catalyzed lignin degradation has been evaluated extensively [24].

3 Textile Applications

Enzymes are principally classified and named according to the chemical reaction they catalyze, as this is the specific property that distinguishes one enzyme from another. In other words, they are named by the substrate on which they act. An enzyme name is assigned not to a single enzyme protein, but to a group of proteins with the same catalytic property, even if they are obtained from different sources. Some of the common types of enzymes and their specific fields of application are listed in Table 3. [82, 84]. Specific enzymes, alone or as mixture, are used in various textile-processing steps as shown in Table 4 [38].

The roles of surfactants and mechanical agitation are related both to the enzyme structures and to the characteristic structure of cotton. The presence of nonionic surfactants in the enzymatic solutions favors enzymes' biological functions. They are compatible with enzymes, whereas anionic and cationic surfactants may form complexes with enzymes. Mechanical agitation can increase apparent enzyme

Table 3 Enzymes used in textile processing

Name	Nomenclature	Textile application	Mechanism
Amylase	EC 3.2.1	Starch desizing	Split starch (amylase) into dextrin and sugars
Catalases	EC 1.11.1.6	Peroxide bleaching after-wash	In situ peroxide decomposition
Cellulase	EC 3.2.1.4	Stone washing, biofinishing for handle modification, carbonization of wool	Degrade cellulose to soluble products
Laccases	EC 1.10.3.2	Discoloration of textile effluent bleaching of lignin-contained fibers and indigo in denim fabric	Degrade a wide range of recalcitrant (unruly) organic compounds including lignin
Lipases	EC 3.1.1.3	Improve hydrophilicity of polyester as a substitute for alkaline hydrolysis Added in detergent	Split fats and oils into glycerol and fatty acids Remove most difficult lipid stains during washing
Proteases	EC 3.4	Removal of protein stains during scouring	Split proteins into soluble polypeptides and amino acids
Pectinases	EC 3.2.1.15	Bioscouring substituting caustic soda boil	Degrade pectin
Oxido-reductase	EC 1	Dyeing	Catalyzes transfer of electrons from one molecule, also called the hydrogen or electron acceptor
Xylanase	EC 3.2.1.8	Bleaching	Degrade linear polysaccharide beta-1,4-xylan into xylose thus breaking down hemicellulose

Table 4 Applicability of enzymes at various textile processing steps

Process	Enzyme
Desizing	Amylase, lipase
Scouring	Pectinase, cellulase, cutinase
Bleaching	Oxidoreductase, xylanase
Dyeing	Oxidoreductase
Finishing	Cellulase, oxidoreductase, lipase
Composting (textile waste)	Laccases, cellulase, protease, nylonase, polyesterase

activity and efficiency in scouring. However, enzymes may be denatured by mechanical agitation with high shear forces [53].

According to the American Soap and Detergent Association (SDA) document, exposure to enzymes may cause irritation and/or respiratory allergies. Skin and eye contact with proteolytic enzymes may cause irritation. Other classes of enzymes are less irritating or pose no risk of irritation. However, formulation ingredients may be irritants. Exposed areas should be protected by using hand and eye protection and other protective fabrications [22].

3.1 Biodesizing

Amylases were the first and most successful enzymes used in the textile industry for desizing. They were first used in the early 1900s when malt extracts from barley containing the active enzymes were applied to greige fabrics. In 1917 bacterial enzymes were isolated and ultimately bacteria became the source for industrial production. The most common size is starch or starch derivatives. This serves as a protective coating on yarns during weaving. After weaving, the size must be removed before dyeing and finishing by treating the fabric with chemicals such as acids, bases, or oxidizing agents. In addition, desizing may be done by amylase enzymes. The enzymatic desizing process is still the main application of amylase in the textile industry, but their application as additives in laundering detergent formulations has increased recently.

Amylases are of two types: dextrinogenic or α-amylases (EC 3.2.1.1), and saccharogenic or β-amylases (EC 3.2.1.2). They are similar in that they hydrolyze glucosidic linkages in the starch molecules, but the point at which the reaction occurs is different [70]. The α-amylase is capable of acting at random locations along the starch chain to break down long-chain carbohydrates, ultimately yielding maltose from amylase, or maltose and glucose from amylopectin. Because it can act anywhere on the substrate, α-amylase tends to be faster-acting than β-amylase and is therefore used for textile desizing. A regular amylase may be applied at a pH 5.5–7.0 and at a temperature of 25–55 °C. Amylases for use at medium temperature can be used in the range of 50–95 °C, whereas high temperature amylase can be used successfully above 95 °C and also in the pad-steam process.

Table 5 Desizing conditions in various machines

Name of machine	Duration	Temp (°C)
Jigger	2–4 ends	60–100
Winch	30 min	90–100
Cold pad-batch	6–24 h	15–40
Hot pad-batch	3–8 h	60–70
Pad-steam	15–120 s	90–110

The end-products of the enzymatic desizing process are various types of sugars and dextrins which are nontoxic. However, they have a negative impact on the BOD of the wastewater.

The desizing process may be divided into three stages: impregnation, incubation, and afterwash. The fabric may be prewashed to remove nonstarch water-soluble additives and to facilitate the binding of amylase to the starch molecules. Thorough wetting and heating to gelatinize the starch facilitates better contact between the enzyme and the substrate. Impregnation should be carried out at temperatures above 70 °C in a buffered solution containing calcium. Alternatively, the fabric may be soaked with the enzyme solution at the optimum temperature before a longer incubation (at a lower temperature) is carried out. The incubation stage may take 2–16 h, depending upon the stability and the activity of the enzyme at the processing temperature and pH, the nature of the size, and of the fabric.

The recommended incubation times in various machines and methods are shown in Table 5 [13]. The amounts used depend on the activity of the product and there are at least two systems for measuring that activity.

Chelating agents are not compatible and should not be used during the enzyme desizing process. Wetting agents and nonionic surfactants can be used to enhance enzyme penetration and adsorption, fiber swelling, and to promote the removal of waxes, soils, and synthetic sizing agents. After enzymatic treatment, the fabrics should be washed off above 80 °C in alkaline liquor followed by a wash in neutral liquor.

Sometimes beef tallow or other fat is added in the size bath to improve the lubricity of the sized yarn after drying. It is, therefore, proposed that lipase enzymes should be included in the amylase desizing bath to catalyze hydrolysis of the fat, the hydrolysis products being glycerol and fatty acid. A synergism between amylase and lipase is possible that results in even more efficient removal of starch than would occur with amylase alone [74].

The requirement for optimal performance of amylase mainly concerns pH, oxidative stability, chelator resistance, and temperature behavior. Modified amylases with improved performance (such as thermostable) are developed by protein engineering methods such as random mutagenesis, homology considerations, and site-directed mutagenesis.

3.2 Bioscouring

Scouring is an alkaline cleaning process for raw fibers (mostly natural) before the coloration process. Bioscouring has a number of potential advantages over traditional scouring. It is performed at neutral pH, which reduces total water consumption, the treated yarn/fabrics retain their strength properties, the weight loss is reduced or limited compared with processing in traditional ways, and it increases cotton fiber softness. The temperature of bioscouring is much lower compared to classical scouring; the optimal temperature is from 40 to 60 °C. Bioscouring can create the desired hydrophilicity in the cotton fabric, but at the same time leave sufficient wax materials on the fabric surface to lessen the required addition of softeners for consumer satisfaction.

However, due to relatively low treatment temperature, the waxes are not entirely removed. The attained degree of whiteness is lower compared to alkaline-scoured or even desized fabric. The seed-coat fragments also do not swell and are not bleached in bleaching [91]. The complex chemical and physical structures of cotton seed-coat fragments ensure that their removal and/or discolorization by enzymes is not easy. Cellulases can be used to clip fibers from the fragments, enhancing their tendency to fall off and cellulases can also help to open up the fragments to further chemical attack. If a chelating agent such as EDTA is added to hemicellulase and xylanase enzymes, then the seed-coat fragments are hydrolyzed much faster than the cotton fabric itself.

For enzymatic scouring, pectinase is the only enzyme needed for wettability, although other enzymes may have beneficial effects. Pectinases are a complex group of enzymes involved in the degradation of pectic substances. They are generally a mixture of enzymes. There are three major classes of pectin degrading enzymes: pectin esterases (PEs), polygalacturonases (PGs), and polygalacturonate lyases (PGLs).

Pectin esterases are mainly produced in plants such as banana, citrus fruits, and tomato, but also by bacteria and fungi [36]. They catalyze hydrolysis of pectin methyl esters, forming pectic acid.

An extremely powerful alkaline pectinase has been isolated recently. The major benefit of this enzyme in bio preparation is that the enzyme does not destroy the cellulose of the cotton fiber. The enzyme is a pectate lyase, and as such very rapidly catalyzes hydrolysis of salts of polygalacturonic acids (pectins) in the primary wall matrix. Pectinase, as the name suggests, hydrolyzes pectin present in cotton as a noncellulosic impurity. The best kinds of pectinase are those that can function under slightly alkaline conditions even in the presence of chelating agents. Such enzymes are called “alkaline pectinases”. Most conventional pectinases are usually inactive under these commercially useful conditions, their optimum activity lying in the slightly acidic region [87].

A study by Sawada et al. [78] shows that the use of a mixture of nonionic surfactants having an HLB value of 13 and a natural organic solvent, D-limonene, greatly increases the scouring efficiency of the pectinase enzyme system obtained from *Aspergillus niger*. Further work [79] showed that the disadvantages of the above aqueous bioscouring process can be minimized by using a reverse micellar system (RMS).

Cellulases are specially suited for scouring of cotton fabrics. Some pectinase enzyme preparations contain cellulase. Those impurities are then removed by subsequent washing. However, the combined actions of both types give greater weight loss and strength loss as compared to the action of pectinase or lipase alone. Cotton fibers, or their blends with other fibers, can be treated with aqueous solutions containing protopectinases for 18 h at 40 °C to give scoured yarn with good tensile strength retention. Pectinases and cellulases are very effective compared to the proteases and lipases. The change in water absorbency of cotton is rapidly catalyzed by pectinases, cellulases, or their mixtures. Pectinases can destroy the cuticle structure by digesting the inner layer of pectins in the cotton cuticle. Cellulases can destroy the cuticle structure by digesting the primary wall cellulose immediately under the cotton cuticle. Cellulases break the linkage from the cellulose side and pectinases break the linkage from the cuticle side. The result of the synergism is a more effective scouring in both the speed and evenness of the treatment. The destruction of the cuticle during enzymatic scouring of cotton was revealed by scanning electron microscopy (SEM) photographs [53].

The combined enzyme system for simultaneous desizing and scouring may contain amylase, lipase, and pectinase enzymes to achieve the necessary fabric properties without the use of harsh chemicals [43].

BioPrep 3000L (Novo Nordisk, Denmark) is an alkaline pectinase, free from cellulases [48]. It works optimally at pH 7–9.5 and at temperature up to 60 °C in exhaust systems and at somewhat higher temperature in pad systems.

A successful strategy for the combined use of α-amylase and hemicellulase/pectinase in the pretreatment of cotton has been developed [64]. The pectin and hemicellulose degrading enzymes are added to the desizing liquor. In addition to desizing, the removal of undesired substances can be fulfilled in one step. In the subsequent bleaching step residual hydrophobic components such as fats and waxes can be mobilized and removed. It can be shown that the enzymatic pretreated cotton has similar or even better properties after a hot bleaching than the conventional desized and alkaline-scoured material.

A study by Sancar et al. [75] showed that application time, water, and energy can be saved by using amylase and pectinase in the same bath, but bleaching by laccase enzyme is not sufficient for fabrics dyed at light shades.

Regarding scouring of cotton fabrics using combinations of pectinase, cellulose, and protease in a single bath, two steps have been carried out with optimum process parameters obtained from these enzymes individually. Absorbency and residual extractable impurity levels are found to be better for multienzyme scouring. Although higher weight losses are observed in the multienzyme scouring treatment, the strength loss of multienzyme scoured samples is not higher than that of samples obtained from individual enzyme scouring. Scaling and adjustment factors identified using Taguchi methods for the above response variables were further substantiated by confirmation tests [77].

Losonczi et al. [55] compared the degradation efficiency of the noncellulosic constituents of cotton in bioscouring with or without EDTA. When EDTA is added in different concentrations to the enzymes, the former does not have any inhibitory or stimulating effect on the main activities, that is, pectinase and xylanase. For enzymatic degradation of cotton seed-coat fragments, EDTA modifies the substrate structure by removing the calcium ions from the crossbridges that link the macromolecules in pectin to one another or pectin to other polysaccharides. EDTA pretreatment significantly decreases the efficiency of enzymatic hydrolysis monitored by reducing sugar liberation, however, simultaneous application of EDTA and enzyme in one treatment bath strongly accelerates the degree of hydrolysis. EDTA applied simultaneously with the enzyme seems to assist in the creation of free and accessible areas for the enzyme present, indicating the synergistic effect of the enzyme and EDTA. However, EDTA pretreatment results in a less accessible substrate for the enzyme applied subsequently, most likely due to the collapse of the temporarily open structure.

Biological oxygen demand (BOD) and chemical oxygen demand (COD) of enzymatic scouring process are 20–45 % as compared to alkaline scouring (100 %). Total dissolved solid (TDS) of the enzymatic scouring process is 20–50 % as compared to alkaline scouring (100 %). Handle is very soft in enzymatic scouring compared to the harsh feel in the alkaline scouring process. Enzymatic scouring makes it possible to scour fabric effectively without negatively affecting the fabric or the environment. It also minimizes health risks in as much as operators are not exposed to aggressive chemicals [68].

Despite all the research on bioscouring, it has yet to be applied on an industrial scale. There is a need for pectinases with higher activity and stability at high temperatures and alkaline conditions. The research on combining cutinases with pectinases to optimize cotton wax removal in shorter processing times, the application of energy (both mechanical and ultrasonic) to significantly speed up the reaction time, and the work with mixtures of hydrolytic and oxidative enzymes derived from solid-state fermentation to attack the seed-coat fragment removal problem all show promise for wider implementation of biopreparation.

3.3 Biobleaching

At the University of Auburn (USA) glucose oxidase enzyme (GOx; EC 1.1.3.4) was used for bleaching when the whiteness index was improved with lower strength loss [83]. In the presence of molecular oxygen, glucose is oxidized by the enzyme glucose oxidase to gluconic acid and hydrogen peroxide. D-Gluconic acid acts as a sequestering agent during bleaching. Amyloglucosidases, pectinases, and glucose oxidases are compatible concerning their active pH and temperature range and were selected. A combination of two or all three preparation steps with minimal amounts of treatment baths and rinsewater showed compatible results in whiteness, absorbency, dyeability, and tensile properties of the treated fabrics.

Recently studies were done of biobleaching of wool under both oxidative and reductive conditions. The studies showed that hydrogen peroxide bleaching in the presence of protease preparation, Bactosol SI (Clariant), considerably improved whiteness and hydrophilicity.

Subtilisins are a family of alkaline serine proteases, generally secreted by a variety of Bacillus species [88]. They catalyze the hydrolysis of peptide and ester bonds through the formation of an acyl–enzyme intermediate. Proteases precisely act on peptide bonds formed by specific amino acids to hydrolyze them. A number of protease enzymes, commercially available on the market, are regularly added to laundry detergents to aid in the removal of protein-based stains. However, they are mostly unstable to hydrogen peroxide. Alkaline proteases with improved stability to peroxide have been subsequently prepared such as Durazyme 16.0L (Novo Nordisk). As no significant whiteness improvement was achieved before 1 h of enzyme addition, it was suggested that the whiteness enhancement effect might be due to initial rapid etching of the wool fibers, making them more susceptible to subsequent bleaching. Hence, it is advisable to pretreat wool before peroxide bleaching so that the enzymes unstable to peroxide can be used. The enzyme treatment may be carried out for 1 h at 50 °C and pH 9.0. The bath is to be cooled to 45 °C before adding hydrogen peroxide and ammonia to pH 8.5–9.0. Whiteness improvement was similar to that obtained in the simultaneous treatment, although slightly inferior. The addition of the protease enzyme (about 0.5–1 %) shortens bleaching time by half for the same whiteness. Similarly, an appreciable increase in whiteness can be achieved under reductive conditions by treating wool with the protease papain, applied in the presence of a mixture of sodium bisulfite and sulfite at pH 6.5–6.9. The process is fairly cheap and rapid as compared to peroxide bleaching, but requires optimization. In both oxidative and reductive modes, a weight loss of at least 3 % can be expected. Although such a weight loss is quite acceptable with cotton when treated with cellulase, it may be excessive for wool, which is much more expensive.

The feasibility of a complete enzymatic one-bath pretreatment of the cotton fabric at low temperature was investigated [90]. The cotton fabric was enzymatic desized, scoured, and bleached simultaneously with an enzyme mixture of starch-degrading enzymes, pectinases, and glucose oxidases. The whole process continued for 2 h at 50 °C, with the final temperature at 85 °C. The process started at pH 5 and increased to 7.5 after 1 h of treatment to activate the generated peracetic acid (PAA) for bleaching. With less time and less use of water and energy, fabrics of good water absorbency, high tenacity at the maximum load, and high degree of polymerization (DP) were obtained and the achieved whiteness was medium.

3.4 Peroxide Killer

Fabrics made from natural fibers such as cotton are normally bleached with hydrogen peroxide before dyeing. Any residual peroxide on the fabric can interfere with the dyeing process. Therefore, a thorough removal of peroxide is necessary.

The traditional method is to treat with reducing agent or thorough rinsing with hot water. Both the methods consume huge amounts of water. The treatment with a small amount of catalase enzyme can also decompose peroxide; the method is easier and quicker.

Catalases (CATs), more correctly hydroperoxidases, catalyze the degradation of H_2O_2 to H_2O and O_2. Catalase or peroxidase is a oxidoreductive class of enzyme produced by a variety of different microorganisms including bacteria and fungi [58] and most have optima at moderate temperatures (20–50 °C) and neutral pH. In addition to the protein part of the molecule, catalase enzyme contains a nonprotein part, which is a derivative of heam and includes metal iron. The advantage of the catalase enzyme [40] is that it attacks only hydrogen peroxide and nothing else. The reaction is as follows:

$$H_2O_2 + \text{catalase} \rightarrow 2H_2O + O_2 + \text{catalase} \tag{1}$$

Peroxidases effectively degrade hydrogen peroxide at varied pH 3–9 and temperature between 30 and 80 °C. The reaction rate is extremely fast and under optimum conditions one mole of catalase is able to decompose 500 million moles of hydrogen peroxide in one minute. The catalase is free to decompose more hydrogen peroxide as long as the desired pH and temperature are maintained. The need to neutralize before adding the dye is beneficial because catalase is most active in the pH range of 6–8.

Normally, when using catalase, the number of rinses can be reduced drastically. Instead of applying catalase in a separate bath prior to dyeing, it may be added in the dyebath 5–10 min prior to adding chemicals and dyes. This is acceptable because catalase acts on hydrogen peroxide only and not on other chemicals or dyes.

The use of a commercial catalase for the elimination of hydrogen peroxide residues from cotton fabrics improved dyeing behavior and the color yield increased considerably with a reactive bifunctional monofluortriazinyl dye [2].

The potential to reuse the peroxide-containing bleaching effluent water for dyeing with reactive dyes was investigated. Bleaching baths were treated prior to dyeing with catalase in order to convert the residual hydrogen peroxide, harmful to the colorants, to water and oxygen. The hydrogen peroxide was completely destroyed by the enzyme, however, the bleaching bath formulation caused unacceptable color changes in the dyed fabrics.

Novozymes performed two life cycle assessment (LCA) studies in China [60]. One study comprises comparison of bioscouring and conventional scouring, and the other by varying dyeing processes (dye, salt, and alkali) and enzyme concentrations. It was demonstrated that by increasing the amount of these components to certain optimum levels, the color difference could be reduced significantly [93]. The resource consumption and environmental impacts induced by enzyme production are generally very small compared with the savings. A small amount of enzyme saves considerable amounts of energy and water in both processes and also aggressive chemicals in the scouring process. The enzymes were transported from a long distance, but considering its quantity, the consequent impact on the environment is not significant.

In the future, the combining of different enzymatic processes in the same bath, such as combined dyeing and biopolishing, combined bioscouring and biopolishing, and combined desizing and bioscouring will help to save more water, time, and ultimately costs.

3.5 Biofinishing

Cellulases are well established in textile wet processing as agents for fiber surface modification. The use of the enzymes on cotton provides a softer finish and a different surface appearance. The main advantage of biopolishing is the prevention of pilling [51]. Cellulases hydrolyze the microfibrils (hairs or fuzz) protruding from the surface of yarn because they are most susceptible to enzymatic attack. A ball of fuzz is called a pill and these pills can present a serious quality problem because they result in an unattractive knotty fabric appearance. After biopolishing fabric shows a much lower pilling tendency. Other benefits of removing fuzz are a softer and smoother handle and better color brightness. The other way to remove fuzz is gas singeing. Hence, the use of enzymes saves gas and emissions from the combustion process.

Cellulase has various effects on man-made cellulosic fabrics such as lyocell (Tencel), viscose, and cellulose acetate. On both viscose and lyocell, cellulase alters the handle and drapeability, and removes surface fuzz. Cellulase also reduces the tendency of viscose to pill and reduces fibrillation of lyocell, but on cellulose acetate the effects tend to be less. Linen was the most susceptible to enzymatic hydrolysis, followed by viscose, cotton, and lyocell [19].

The cellulases used are chemically complex and consist of at least three enzyme systems working synergistically together.

(1) Endo-β-(1,4)-gluconases (EG) or endocellulases that hydrolyze cellulose chain molecules randomly, preferentially attacking the internal regions of the polymer.
(2) Exo-β-(1,4)-gluconases or cellobiohydrolases that hydrolyze cellulose chain ends to produce cellobiose. These exo-cellulases may assist disintegration of crystalline regions, making the region more susceptible to hydrolysis by endo-cellulases.
(3) The third enzyme, β-(1,4)-glucosidase then hydrolyze cellobiose and other small oligomers into glucose [38].

The different effects can be obtained with different enzyme compositions: endoglucanase (EG) or EG-rich preparations are best for ageing and defibrillation of fiber surfaces, whereas complete cellulase systems are best for cleaning and depilling effects [19].

The surface appearance and feel of fabrics produced from the new cellulosic fiber, Tencel, can be enhanced by cellulase treatment. Laboratory-scale studies have been carried out using purified Trichoderma reesei cellulase components to determine which enzymes provide some benefit and which cause detrimental effects on Tencel fiber. Two enzymes were identified as beneficial and this information was used to produce new commercial cellulase products, using genetic engineering to remove detrimental components and increase amounts of the beneficial enzyme components [35].

Two types of cellulases commonly used are:

(1) Acid cellulases having greatest activity in the pH range 4.5–5.5 at 45–55 °C
(2) Neutral cellulases require a pH of 5.5–8.0 at 50–60 °C.

Surface modification of cellulosic fabrics conferring a cooler and softer feel, brighter luminous color, and more resistance to pilling using cellulases, is often known as biopolishing,,a term created by Novo Nordisk. For cotton, the restriction of the enzyme to the fiber surface is easily achieved, because cellulose is a highly crystalline material and possesses only a small amorphous region, making the diffusion of enzymes into the interior of the fiber nearly impossible. Thus, by regulating enzyme dosage and choosing the right type of enzyme, the catalytic action of the enzyme can be confined to the surface of cotton and to the amorphous regions, leaving the fibers, as a whole, intact.

The elimination of superficial microfibrils of the cotton fiber through the action of cellulase enzymes is obtained by the controlled partial hydrolysis of cellulose followed by mechanical treatment, leaving the surface of the fibers free and conferring a more even look. The improvements in fabric softness and smoothness are permanent in contrast to the softeners applied to the fiber surface. Moreover, the water regain is not hampered by the enzymatic treatment as in case of most softeners. Although biopolishing may be carried out at any time during wet processing, it is most conveniently performed after bleaching. Treating fabrics with enzyme after dyeing may affect the shade, so some adjustment in dye formulation may be necessary. It may also be performed in garment form. Batch processing using washers, jets, becks, and winches is extremely suitable, as pH and temperature can be controlled easily.

Controlled finishing with cellulase enzyme optimizes surface properties of the fabric, but causes a decrease in tensile strength. Commercially a weight loss of 3–6 % and strength loss of about 10 % is considered acceptable. It is also found that cellulase is more active in mercerized cotton than in either 100 % cotton or cotton/polyester blends [37].

The effect of cellulase enzyme treatment followed by the dyeing process on the low-stress mechanical properties of the linen fabric was investigated [42]. The low-stress mechanical properties including the tensile, shearing, bending, compression, and surface properties of linen fabrics altered after enzyme treatment and subsequent dyeing to a greater extent, depending predominantly on the concentration of enzyme used.

During finishing by cellulases strong mechanical agitation of the fabric is provided by some means, for example, rotating-drum washers and jets. Mechanical actions, in the form of agitations, between fabric and equipment or surface-to-surface contact of fabrics enhance the reactivity of enzymes by improving two-way diffusions and also the efficiency of the processes. With the increase in mechanical actions, the dissociation of bound enzymes increases [16]. Various levels of agitation are employed in pad-batch, winch machines, and jet systems in practice. However, increasing levels of agitation also reduce the adsorption of enzymes, increase the number of free sites for enzyme hydrolysis, and in extreme cases mechanical actions, usually, reduce catalytic specificity of the cellulases. Effects of agitation on individual component enzymes have also been used to investigate the reaction mechanism of component enzymes in crude mixtures of cellulases. Without mechanical agitation, inferior results have been reported in biopolishing [67].

3.6 Denim Biowash

Indigo dye has poor substantivity for cellulose and hence, it mostly remains at the surface of the fiber after dyeing and as such is called ring dyed. Such ring-dyed materials are subjected to treatment with stone or enzymes, which remove dyes randomly from the abraded portions of the fabric exposing white surfaces. This popular style is utilized in “faded jeans”. Microscopy reveals that for indigo dyeing, the extent of the penetration of the colorant into the cross-section of the cotton yarn depends on the pH of the bath. When the pH of the dyebath is decreased from 13 to 11, the yarn progressively becomes ring dyed. Associated with the increasing ring dyeing, more color yield is obtained making the wash-down process easier. The highest color yield was observed within the pH range of 10.8–11.2.

Denim garments are made from warp face cotton fabric in which warp yarns are dyed with indigo dyes. These garments are subjected to a wash treatment to give them a worn look. In the traditional stonewashing process, the blue denim is faded by the abrasive action of pumice stones. Cellulases were first introduced in the 1980s and nowadays more than 80 % of denim finishers use cellulases or a combination of stones and cellulases to create the worn look on denim. Cellulases work by loosening the indigo dye on the denim in a process known as “biostoning”. This treatment can be applied to knit and woven cellulosic fabrics such as cotton, viscose, linen, and their blends. An enzymatic stone-wash process requires equipment with sufficient shear forces and mixing, such as a drum washer.

The conventional denim wash process consists of treatment with pumice stones. About 1 kg stone is required for 1 kg of denim fabric. A large amount of pumice sludge is produced in this process. For example, a denim finisher processing 100,000 garments a week with stones typically generates 18 tons of sludge [7]. This may block drains so it needs to be filtered out of wastewater. An environmental assessment was performed on jeans [62]; the biostoning process produces very little sludge and is proved to be more environmentally friendly than the traditional stoning process using pumice.

Often irreversible inactivation of the enzyme at the end of the application is beneficial because ongoing enzymatic action may lead to undesired effects such as extended tensile loss and over-performance in the case of cellulase application. Inactivation of the enzyme can be easily realized by shifting the pH (above 10 for 5–10 min) and temperature (above 80 °C) to extreme values for a relatively short period.

More recently, some authors showed that laccase (with and without using a mediator) is an effective agent for stonewashing effects of denim fabric [69].

3.7 Shrinkproofing for Wool

Various finishing effects on wool can be obtained by the use of enzymes in more environmentally friendly ways than traditional chemical processes. However, the complexity of wool fiber makes it difficult to find enzymes that are able to modify some of the properties of wool efficiently, while not excessively damaging its structure [73].

Due to the presence of scales on the surface of the wool fibers, frictional resistances on the two directions along the fiber axes are different. This causes fibers to entangle and shrink during agitation of the fiber mass. A process conventionally used for wool shrinkproofing is chlorination. This process degrades the exo-cuticle of the wool, forming cysteic acid residues and protein losses. This process has been replaced by proteinase enzyme treatment due to their high specificity and much lower environmental impact. However, proteinase treatment leads to protein degradation, resulting in deterioration of fiber strength and limited shrink resistance [10]. Several reports show that increasing enzyme size by chemical crosslinking with glutaraldehyde or by the attachment of synthetic polymers such as polyethylene glycol can reduce enzyme penetration and the consequent reduction of strength and weight loss [80]. Some of these processes have been tested on an industrial process scale [85].

Some researchers describe methods to improve the shrink resistance of wool by pretreating with a gentler oxidizing agent, such as H_2O_2, and then with protease enzyme [103]. Others refer to processes to achieve shrink resistance by treating wool with a protease followed by a heat treatment [15].

By bleaching wool with hydrogen peroxide in the presence of imino disuccinic acid sodium salt (IDAS), a new environmentally friendly chelating agent followed by treatment with lipoprotein lipase enzyme at 50 °C and pH 7 for 1 h, it is possible to obtain machine-washable, pilling-resistant wool without severe loss to the fiber strength. Some properties of wool, such as shrinkproofing, antipilling, and dyeability (towards anionic and reactive dyes) are improved. The degree of whiteness and wettability of the preoxidized wool fabrics was enhanced [21].

The treatment with 1 % enzyme (subtilisin serine alkaline protease) and 1.4 % sodium sulfite, applied for 30 min gives complete shrinkage control with strength retention and 3.71 % weight loss [11].

The screening for new protease-producing microorganisms with high specificity for cuticles is being investigated as an alternative for the existing proteases [23]. Papain is the best-known cysteine protease. It was isolated in 1879 from the fruits of Carica papaya. The optimal activity of papain occurs at pH 5.8–7.0 and at temperature 50–57 °C, when casein is used as the substrate [41].

A patent application about the use of laccase from T. versicolor plus a mediator to increase the shrink resistance of wool has been published [101]. Also, Lantto et al. [49] found that wool fibers can be activated with laccase if a suitable mediator is present. Therefore, the use of laccase for antishrink treatment of wool seems very promising.

The effect of enzyme treatment (savinase, resinase, xylanase, and pectinase) on the physical, chemical, and structural properties of wool and specialty hair fibers was evaluated [18]. It was observed that xylanase and pectinase treatments had as good a cleaning efficiency as conventional soap scouring. Furthermore, at the concentrations used, neither of these two enzymes caused any physical damage to the fibers, as confirmed by the tenacity and diameter values, and SEM pictures. The effectiveness of resinase as a scouring agent was, however, not very satisfactory. Because specialty hair fibers possess very few impurities compared with sheep wool, the milder treatment conditions would be very appropriate for the treatment of these fibers.

The presence of any one of the three proteolytic enzymes in the dyebath increases the amount of dye absorbed in all the dyeing processes studied. The action of the enzymes on increasing the dye absorption becomes more evident when the dyeing temperature is lower and this action is greatest when the temperature gets closer to that of the maximum activity of the enzyme (around 50 °C; [73].

3.8 Degumming of Silk

Enzyme degumming of silk is regularly used in China. The treatment time is somewhat longer than with synthetic detergent, but shorter than soap. It is considered to have a mild action on the fibers and is claimed to produce uniformly degummed material with soft handle and reduced lousiness. The recommended proteolytic enzymes are trypsin (of animal origin), pepsin, and papain (of vegetable origin). They hydrolyze peptide bonds formed by the carboxyl groups of lysine and arginine. Enzymatic degumming is not a single-step process. The gum must be swollen before the enzyme treatment. An additional treatment with mild alkali is necessary to remove natural wax, soil, and lubricant oils.

Trypsin, a proteolytic enzyme secreted by the pancreas, is most active at pH range 7–9. Ammonium bicarbonate (0.1 mol/l) is considered to be a good buffer. For tryptic digestion, 1–2 % enzyme on the weight of material at 37 °C for 1–4 h is considered appropriate.

Papain is used for boiling off cocoons and degumming of silk. Papain, obtained from a vegetable source, papyrus latex, is most active at pH between 5 and 7.5 at 70–90°C. Original poisonous activators potassium cyanide or hydrogen sulfide are being replaced with sodium thiosulfate, alone or as an admixture with sodium hydrosulfide.

Several alkaline, acidic, and neutral proteases that dissolve sericin without affecting silk fiber protein, have been studied as degumming agents [5]. Alkaline proteases seem to be the best for removing sericin and improving silk surface properties including handle, shine, and smoothness [4], although they are not in commercial use.

A bacterial enzyme, alkalase, is very effective in hydrolyzing sericin. It may completely hydrolyze sericin in 1 h at 60 °C and pH 9.

3.9 Degumming of Ramie

Ramie fiber is obtained from the skin of a high fiber productivity perennial herbaceous plant, Boehmeria nivea (Linn.) Gaudich. It is widely used in textiles and the biomass industry (biocomposite, biofuel, etc.). But ramie fiber could only be used if most of the noncellulose materials are removed by degumming. Its utilization is limited today because the traditional chemical degumming process causes serious environment pollution, high energy consumption, high production cost, and fiber damage.

A study [54] revealed that over 90 % of the gum in raw ramie could be removed only with Pectobacterium sp. CXJZU-120 in 6 h. The rapid process was not only suitable for the extraction of ramie fibers from different grades of raw material and retaining the inherent morphological structures and textile properties, but also could reduce production cost up to 20.5 %, raise resource utilization by more than 50 %, and reduce pollution charge by more than 80 % compared with traditional chemical degumming.

Ca^{2+}-activated composite enzyme (pectatelyase/hemicellulase/laccase) was employed to degum ramie fiber. The gum, hemicellulose, and lignin were removed effectively and treated fibers had the typical cellulose I structure suitable for direct textile and other applications. The fiber fineness, breaking strength, whiteness, and residual gum of fibers improved greatly. Flux fiber may also be degummed by this environmentally friendly technique [104]

3.10 Surface Modification of Synthetic Fibers

Synthetic fibers share common disadvantages, such as high hydrophobicity and crystallinity, that affect not only wearing comfort (making these fibers less suitable to be in contact with human skin), but also processing of fibers, impeding the application of finishing compounds and coloring agents. Classical methodologies to improve fiber hydrophilicity, such as alkaline or acid hydrolysis, lead to the deterioration of fiber properties such as irreversible yellowing and loss of resistance. Recent studies show that surface modification and hydrolysis of polyester and polyamide with enzyme are environmentally benign methods. The major advantages of polymer modification with enzyme as compared to chemical methods are milder reaction conditions and highly specific nondestructive transformations, targeted to less fiber damage.

Synthetic materials are generally considered resistant to biodegradation. However, fairly recently it has been established that enzymes are also able to act on synthetic materials. The advantage of enzymes over conventional techniques is that the favorable bulk properties of PET are not affected because the enzymes are too big to penetrate into the bulk phase of the material. Various research groups assessed the potential of laccases, lipases, polyesterases (serine esterase), and cutinases in the oxidation or hydrolysis of polyester materials

A polyesterase was reported by Yoon et al. [102], for surface modification of PET and polytrimethyleneterephthalate (PTT). The authors reported that the formation of terephthalic acid (a hydrolysis product) could be monitored at 240 nm. The enzymatic treatment resulted in significant depilling, efficient desizing, increased hydrophilicity and reactivity with cationic dyes, and improved oily stain release [102]. Recently, Nechwatal et al. [59] tested several commercial lipases/esterases for their ability to hydrolyze oligomers formed during the manufacture of PET, which may otherwise create problems after dyeing by deposition on machines and fibers.

Cutinase, lipases, and polyesterases increase hydrophilicity by actual hydrolysis of PET, whereas laccases oxidize the polyester surface. Cutinases (EC 3.1.1.74) are serine hydrolases that can accept a wide range of substrates such as poly(ethylene terephthalate) and polyamide. Crystallinity greatly affects the capability of cutinase to hydrolyze the ester bonds. Cutinase displays relatively high activity towards amorphous polyester and little activity on highly crystalline substrates [61]. The structure and properties of cutinases are well described by Carvalho et al. [12]. In contrast to lipases, cutinases do not require interfacial activation; the active site is accessible because it does not have a lid, and the oxyanion hole is preformed but considerably flexible in solution. Cutinases seem to have a large potential in the enzymatic surface modification of polyester. The optimum pH and temperature for cutinase from Fusarium solani pisi are 8–8.5 and 25 °C; above 35 °C the activity decreases rapidly. Novoenzymes improved temperature stability to as high as 65–80 °C. Cutinase or lipase treatment does not result in pitting corrosion, as in the case of alkaline treatment; surface treatment is more or less homogeneous. However, cutinase strongly adsorbs to the polyester surface. The adsorbed enzyme can be removed by using proteases or using a thorough washing and extraction method.

Due to poor hydrophilicity, textile materials made from polyamide 6,6 are also uncomfortable to wear. It leads to static cling and stain retention during laundering. The fiber is unsuitable for specific finishing treatments such as coupling of flame-retardant or covalent immobilization of proteins. Biocatalytic processes have been developed to modify polyamide surfaces enhancing hydrophilicity. Enzymes that are able to hydrolyze polyamide surfaces are proteases, amidases, and cutinase [32]. The hydrolysis of polyamide is based on breakage of the amide linkages of the polymer surface resulting in amino and carboxylic groups yielding. In addition to hydrolytic enzymes, oxidases from lignolytic fungi have been shown to depolymerize polyamides. Nylon-degrading peroxidases attack methylene groups adjacent to the nitrogen atoms and reaction then proceeds in an auto-oxidative manner.

A study by Parvinzadeh [66] confirms the structural changes of nylon 6 fibers using Subtilisins protease by measuring the dyeability, hydrophilicity, chemical changes, and fastness properties.

The enhancement of the hydrophilicity of synthetic polymers such as polyester and polyamide is a key requirement for many applications ranging from electronics to functional and technical textiles. The new functionalized fibers can have a totally new range of applications such as filter media, smart, technical, and high-performance materials. Future challenges are in the area of improved activity and better temperature stability. Despite some achievement, the potential benefits of enzymatic modification of synthetic fibers are far from being fully explored [89].

For acrylic and cellulose acetate fibers enzymes can be used to accomplish the formation of reactive and/or hydrophilic groups at the surface by hydrolysis of their pendant groups without affecting, in theory, the integrity of the main chain of the polymer. The pendant group in polyacrylonitrile (PAN) is the nitrile group. The ester group of the polysaccharide substituent is a potential supplier to hydrolyze the cellulose acetate fibers in a controlled manner, creating hydroxyl groups at the surface. The modification of PAN and cellulose acetate with enzymes results in two types of products: soluble compounds and new chemical groups attached to insoluble fiber substrate. For PAN fiber, only nitrilase and amidase generate a soluble product, ammonia; nitrile hydratases generate amide groups as new sidechains of the PAN main chain. For cellulose acetate, the hydrolysis of its sidechains releases acetic acid to the reaction media and the hydroxyl group is located on the polymer backbone.

The surface of PAN was modified by nitrile hydratase and amidase enzymes obtained from different sources (Rhodococcus rhodochrous and A. tumefaciens). After enzymatic treatment the fabric became more hydrophilic and the adsorption of dye was enhanced [26].

Although there is no industrial application yet, the research results demonstrate that enzymatic treatment of PAN would give advantages in the quality of treated fibers, as well as in energy saving and pollution control [5].

Despite different substrates, origin, and amount of enzyme used, it is possible to specifically modify the nitriles of PAN into amides or carboxylic groups at moderate temperature and pH conditions with distinct chemical properties. Several aspects including staining properties and hydrophilicity are clearly improved for PAN fibers. Owing to its excellent mechanical properties, stability, and low cost, modified PAN is also of interest for filters in reverse osmosis, gas separation, protein immobilization, ion exchange, ultrafiltration, and dialysis [56].

3.11 Textile Printing

The possibility of using enzymes in natural and synthetic thickener systems for the printing of cotton and wool has been investigated, in particular the effect on color and surface structure. The efficiency of different enzymes (cellulases, proteases, and laccases) concerning their applicability, that is, their activity and stability within different thickener systems (polysaccharide, acrylic polymer, and their mixtures), was studied. Rheological parameters (viscosity and viscoelasticity) of the printing paste were determined and the color and/or structure effects on the fabric surfaces were assessed.

3.12 Laundering

The main application of amylases is still in the desizing process, but their application as additives in laundering detergent formulations have increased recently. One of the most important criteria for the use of amylase in detergents is to maintain optimal activity under the very oxidizing washing environment. Oxidative stability of α-amylase was achieved by site-directed mutagenesis, replacing oxidation-sensitive amino acids such as cysteines and methionines with nonoxidizable residues. Two currently available oxidative stable α-amylases are Purastar OxAm (Genencor) and Duramyl (Novozymes).

Modern detergents contain a sophisticated mixture of enzymes to remove stains and to assist cleaning at low temperature. Proteases, lipases, and amylases are generally used to assist the removal of stains. Cellulase assists in the removal of particulate soils by removing microfibrils from the cellulosic fabrics. Generally, the detergents for this purpose rely on a mixture of enzymes, strong sequestering agents, and soil-release polymers to provide satisfactory stain removal and soft finish. Although the short fiber ends are hydrolyzed by enzymes, additional mechanical agitation is necessary to complete the process of hydrolysis and removal of hydrolyzed products from the fabric surface, which is best attained in rotating drum washers and jets.

The effectiveness of a few types of enzymes in removing some common stains is summarized in Table 6 [72].

Enzymes can easily digest protein stains, however, oily and fatty stains have always been troublesome to remove. The trend towards lower washing temperatures has made the removal of grease spots an even bigger problem. This applies particularly to materials made up of a blend of cotton and polyester. The lipase is capable of removing fat or lipid and fatty stains such as fats, butter, salad oil, sauces, and the tough stains on collars and cuffs [83].

Table 6 Enzymes and their effectiveness as stain removers

Name of enzyme	Effective as stain remover for
Proteases	Grass, blood, egg, sweat stains
Lipases	Lipstick, butter, salad oil, sauces
Amylases	Spaghetti, custard, chocolate
Cellulases	Color brightening, softening, soil removal

3.13 Enzyme-Assisted Dye Manufacture

Before the invention of synthetic dyes, many textile dyes (indigo, madder, wood, etc.) were manufactured by fermentation of plants. Many microorganisms produce pigments during their growth, which are substantive as indicated by the permanent staining that is often associated with mildew growth on textiles and plastics. Some microbial pigments are benzoquinone, naphthoquinone, anthraquinone, perinaphthenone, and benzofluoanthene quinine derivatives resembling the vat class of dyes. Microorganisms seem to offer great potential for the direct production of novel textile dyes or dye intermediates by controlled fermentation techniques substituting chemical synthesis.

3.14 Biological Effluent Treatment

Biodegradable organic matter is utilized by natural microorganisms during metabolic processes as their source of food and energy. Municipal wastewater, industrial effluents, and agricultural (irrigation) return waters are some of the sources of oxygen-demanding substances. These biodegradable substances include starch, fat, protein, acid, alcohol, aldehyde, ester, and the like. The aerobic metabolism of aquatic microorganisms predominates when oxygen is available. The end products of such metabolisms are more or less nonobjectionable. One major disadvantage of aerobic digester is that it generates a considerable amount of sludge.

As soon as the dissolve oxygen level drops, fish and other aquatic lives are threatened and in extreme cases, killed. Subsequently in an oxygen-depleted environment, very quickly anaerobic metabolism commences utilizing the remaining food or substrate. In the anaerobic process, which widely occurs in nature, organic substances are degraded mainly into gaseous substances (principally methane or carbon dioxide) and smaller amounts of solid end products than in the case of aerobic digestion. The microbial population, which exists in anaerobic digestion systems, is different from those of aerobic systems and is sensitive to oxygen. A series of metabolic reactions occurs in the absence of oxygen. The end product of such anaerobic metabolism is undesirable and the resulting odor, taste, and color reduce the acceptability and attractiveness of water.

Dyes usually have a synthetic origin and complex aromatic molecular structures that make them more stable and more difficult to biodegrade. A wide range of microorganisms including bacteria, fungi, and algae are capable of efficiently decolorizing a wide range of dyes. Among these microorganisms, fungal biomass can be produced cheaply using relatively simple fermentation techniques and inexpensive growth media. Fungal biomass, which would otherwise be a nonessential product of various industrial fermentation processes, can also be used to remove dyes from dyehouse wastewater. Most research work to date has concentrated on living fungi for biodegradation and biosorption of the dyes. A study by Fu and Viraraghavan [29] showed that dead fungal biomass of Aspergillus niger is effective in removing Acid Blue 29 from aqueous solution. The biomass was pretreated with sulfuric acid at pH 4.0 for 24 h. It was then washed thoroughly to bring the pH to 6.0.

Several enzyme preparations from various fungi have been observed [1] to decolorize triarylmethane, azo, anthraquinone, indigo, and metal chelate dyes. In all preparations, laccase was a predominant enzyme, but lignin peroxidase and/or manganese peroxidase were also present. All were most active at 50 °C and pH 5.0. The discoloration efficiency depended on the source of the enzyme and substrate (dye). Some white-rot fungi (lignin peroxidase, manganese peroxidase, and laccase) have the ability to decolorize textile dyes and the composition of the media affects the result. Fungi can decolorize dyes faster in a nitrogen-limit medium than in a nitrogen-sufficient medium [34].

Azo dyes, even with several azo groups in their structure, are readily decolorized by anaerobic biomass. The removal is not affected by the type of dye used, even at high concentrations. The dispersing agents do not seem to affect the removal of the organic load in any significant way. Anaerobic digestion should be implemented to remove anionic azo dyes and the subsequent color produced by them. The compounds are reduced to aromatic amines, which can be later degraded by an aerobic treatment. Anthraquinone dyes can be removed in 2 or 3 days at a very low concentration (35 mg/l) in order to avoid inhibition of the biomass or else be removed previously by coagulation or flocculation [31]. Special care should be taken in regard to toxic wastes. As such, these must not be subjected to biological treatment or may be pretreated chemically before biological treatment.

Many synthetic dyes, such as azo dyes, are resistant to microbiological degradation under aerobic conditions maintained in common treatment plants. Many dyestuffs, in particular disperse, direct, and basic dyes, are removed from wastewater via adsorption onto activated sludge. However, highly water-soluble reactive and acid dyes are poorly adsorbed on activated sludge.

4 Enzymatic Fictionalization

The surface of textile fabrics may be modified by interacting with enzymes. The objects of such treatments are:

(1) Modification of surface properties of textiles without hampering bulk properties.
(2) Substitution of non-eco-friendly textile functional finishes.
(3) Higher stability, recovery, and reuse of enzymes by immobilization.

4.1 Enzyme Immobilization

An immobilized molecule is one whose movement in space has been restricted either completely or to a small limited region by attachment to a solid structure. The main advantage for enzyme immobilization is the easy separation of the enzyme from the reaction mixture (substrates and products) and its reusability for tens of times, which reduces the enzyme and the enzymatic products cost tremendously [20]. Other advantages are:

(1) Quick start and stop of the reaction by moving the enzyme into and away from the reaction solution, by monitoring reaction conditions thereby enhancing enzyme stability.
(2) Product is not contaminated with the enzyme.
(3) Easy separation of the enzyme from the product

In industrial biotechnology, the skill to stabilize and reuse an enzyme catalyst through immobilization has proven one to be of the key steps in rendering an enzymatic process that is economically viable [105]. Availability of the immobilized enzyme catalyst with improved activity and stability is also expected to reduce the expense of products [65]. Several new types of carriers and technology have been implemented to improve traditional enzyme immobilization, which aimed to enhance enzyme loading, activity, and stability to decrease the enzyme biocatalyst cost in industrial biotechnology. These include crosslinked enzyme aggregates (CLEAs), microwave-assistant immobilization, mesoporous support, and single-enzyme nanoparticles.

In early enzyme immobilization, support was used to insolubilize the enzyme and thus to facilitate its separation and reuse, which provides easy control over the noncatalytical properties of the obtained immobilized enzyme. Thus, with the increased understanding of the correlation of enzyme property with structure and microenvironment, a great number of synthetic or natural carriers of tailor-made chemical and physical properties, with different shapes/sizes, porous/nonporous structures, different aquaphilicities and binding functionalities, have been specifically designed for various bioimmobilization and bioseparation procedures [100].

Epoxy resin carrier shows maximum immobilization and extreme stability in successive cycles comparatively. The immobilized conditions and parameters may influence the activity of immobilized cellulose [46].

Low-cost textile fabrics, made of polyester or polyamide, are alternative carrier materials for the immobilization of enzymes. Low-cost fabrics with a high enzyme load, a high relative reactivity, and good permanence can be produced by photo-induced crosslinking and grafting processes using monochromatic excimer UV lamps.

Depending on the support and the used reactive agent, 20–70 mg enzyme per gram carrier could be fixed. The relative activity of the catalase after the immobilization was 5–20 % of the free, not fixed, catalase. The immobilized enzyme showed even after 20 reuses a distinct activity and the integral activity over all reuses 3.5 times higher than the activity of the free catalase.

Immobilization of various industrial enzymes onto or within the textile matrix can be achieved via adsorption, covalent bonding, and entrapment to get increased activity and stability in various applications as well as to build new functionalized textile products [98]. Immobilization of α-amylase, alkaline pectinase, and laccase enzymes onto ester-crosslinked as well as Cu-chelated cotton fabrics was carried out followed by assessing the degree of antimicrobial activity against Gram-negative and Gram-positive bacteria and fungi. Cu-chelated cotton fabric showed higher activity. Among immobilized enzymes, alkaline pectinase showed highest, α-amylase intermediate, and laccase lowest activity irrespective of the used microorganism. Antimicrobial activity of the treated fabric lasted for more than 10 wash cycles [39].

Antibacterial fictionalization for textile goods may be an effective way to prevent disease transmission with applications in the consumer, military, and healthcare markets. The enzyme, lysozyme, was successfully immobilized onto the surface of wool fabric support by using glutaraldehyde as a crosslinking agent in order better to impart an antibacterial effect to the wool fabric. The maximum activity of immobilized lysozyme was obtained through the optimization of several immobilization parameters [96]. Lysozyme can also be covalently attached to cotton fabrics that are activated via esterification with glycine and glycine dipeptide. For applications in the food industry, lysozyme can be incorporated into chitosan films for controlled release of the enzyme. In addition to lysozyme, oxygen-consuming enzymes may be immobilized in food-packaging materials to prevent microbial growth.

Smart materials are expected to detect changes in the environment and respond with specific actions. The high specificity of enzymes can be exploited for the design of smart materials in two ways. Enzymes can impart novel sophisticated functionalities to materials ranging from antimicrobial effects to self-cleaning or self-detoxifying properties. On the other hand, enzymes can be used as triggers to impart bioresponsive properties to materials containing specific elements susceptible to modification by these biocatalysts. In several areas, smart materials are constructed such that they respond to triggers (e.g., enzymes) allowing a controlled release of active agents (such as drugs and perfumes). Many active agents in pharmaceuticals, food, and agriculture require temporal stabilization and protection against degradation or oxidation. In addition, the efficacy of such agents may be improved by increasing their solubility or by masking unwanted properties, such as toxicity or bad taste, at least before the target environment is reached. Finally a sustained or triggered release may be required. A natural or synthetic polymer may be judiciously combined with a drug or other active agent in such a way that the active agent is released from the material in a predesigned manner. Enzyme immobilization onto textiles was used to create smart materials with novel properties such as self-detoxifying or antimicrobial activity. For military purposes, organophosphorous hydrolase was covalently immobilized on cotton for detoxification of organophosphorous warfare agents.

Textiles with antimicrobial properties have been produced by immobilization of a variety of enzymes. Attachment of alkaline pectinase, alpha-amylase, or laccase

Table 7 immobilisation of various enzymes on fabrics

Enzyme	Fabric type	Activation/binding material
Peroxidase (HRP)	Polyester, polyethylene	Glutaraldehyde, plasma
Catalase	Polyester, polyamide 6,6	Photochemical
Catalase	Cotton	Oxidation by sodium periodate
Tyrosinase	Silk fibroin, polyamide 6,6	Glutaraldehyde
Laccase	Polyamide 6,6	Enzymatic hydrolysis, Glutaraldehyde, and spacer
Glucose oxidase	Silk fibroin, polyamide 6, viscose, polyester, polypropylene	Various activation strategies
Alkaline phosphatase	Silk fibroin	Low-temperature plasma
Lysozyme	Cotton	Esterification with glycine/glutaraldehyde
	Wool	Glutaraldehyde
Organophosphate hydrolase	cotton	Esterification with glycine/glutaraldehyde
Thrombin	Polyester	Ethylenediamine

leads to antimicrobial fabrics retaining full activity for at least 10 consecutive wash cycles [39].

Fabrics are increasingly gaining importance as supports for enzyme immobilization. Various strategies have been developed for incorporation of enzymes into polymers including entrapment, covalent attachment, and adsorptive binding. Polydimethylsiloxanes have been used for covalent attachment of enzymes including lipases and proteases. Plasma treatment has been used for activation of polyethylene, whereas polyester and polyamide are activated photochemically. Polypropylene can also be activated with polyaniline using ammonium persulfate as the oxidizer. This pretreatment greatly facilitated both adsorptive and covalent immobilization of proteins such as HRP.

Wehrschűtz-Sigl et al. [97] summarized strategies followed by various researchers for immobilization of enzymes (Table 7) using a variety of fabrics.

Peroxidase (HRP) immobilized on nonwoven polyester fabrics in the presence of glutaraldehyde as a crosslinking agent retained 85 % of its activity after 4 weeks of storage at 4 °C whereas free enzymes loses 90 % of its activity under the same condition. Catalase is widely used for textile bleaching and sterilization of liquid food products by conversion of residual peroxide to oxygen and water. Apart from various inorganic carrier materials, fabrics have been used for catalase immobilization. Catalase was photochemically immobilized on polyester and polyamide 6, 6 using diallylphalate or cyclohexane-1, 4-dimethanoldivinylether as the crosslinking agent. The immobilized enzyme was highly stable with a 3.5 higher activity after 20 cycles when compared to free enzyme [63].

For effluent treatment and other applications, laccase has been immobilized on inorganic carrier materials such as alumina pellets. Recently laccase has been bound to organic polymers (i.e., PEG) to obtain water-soluble immobilized proteins with enlarged molecular weight and modified sorption properties. Such constructs have been used in detergent to prevent dye transfer. A novel method of laccase immobilization on polyamide 6, 6 involved limited surface hydrolysis of polyamide 6, 6 by protease to introduce functional groups. Thereafter first the spacer 1, 6 hexanediamine followed by laccse were attached by glutaraldehyde.

In most traditional systems, the control of release and the stabilization of the agent are based on encapsulation. There are three primary mechanisms by which active agents can be released from this kind of delivery system: diffusion, swelling followed by diffusion, and degradation. Diffusion occurs when a drug or other active agent passes from the polymer matrix into the external environment through the polymer that forms the controlled release system. Because polymer coating is essentially uniform and of an unchanging thickness, the diffusion rate of the active agent can be kept fairly stable throughout the lifetime of the delivery system. The diffusion can occur on a macroscopic scale, as through pores in the polymer matrix, or on a molecular level, by passing between polymer chains. Most systems are designed to control the kinetics of release of the active agent in a site- and time-dependent manner. The release of the active agent can be triggered by the local conditions in the target environment. Much effort is focused on creating biodegradable polymers for enzymatic drug delivery systems that permit release of the entrapped drug only during degradation of polymer matrix. Another possibility is the preparation of films of different enzymatically degradable polymer such as chitosan.

5 Future Trends

During the last few years, enzymes have been thoroughly studied and used in order to develop environmentally friendly alternative processes for almost all steps in textile processing. There are already some commercially successful applications, such as amylase used for desizing, cellulose and laccases for denim finishing, and proteases incorporated in detergent formulations.

Although some enzymes already play an important role in textile processing, their potential is much higher and their applications are likely to increase in the future. Productivity and efficiency are to be improved so that these biotechnologies become economically advantageous over conventional approaches. Further research is necessary for biomodification of synthetic and natural fibers of improved properties. New approaches are needed to understand the metabolism and growth of the host organism better.

Genetic engineering offers new opportunities to produce modified or new enzymes with better properties. The use of genetically modified microbial enzymes of commercial importance can be expected to expand into many other areas of the textile industry thus replacing existing chemical or mechanical processes in the near future [14].

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Regenerated Cellulosic Fibers and Their Implications on Sustainability

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Abstract This chapter discusses the present scenario and market trend of regenerated cellulosic fibers, and the properties of principal fibers existing in the market as well as some new fibers recently developed and yet to be explored. Production technologies of these fibers are discussed and their potential applications are presented. Various sustainability issues related to the production of regenerated cellulosic fibers are dealt within this chapter. The last section discusses the results of research studies conducted to assess the environmental impacts and sustainability aspects of regenerated cellulose fibers.

Keywords Regenerated cellulosic fibers · Production · Processing · Applications · Lifecycle assessment · Sustainability

1 Introduction

1.1 *Present Scenario and Market Trend*

Among the various regenerated cellulosic fibers, viscose rayon is mostly used in the textile industry and accounts for roughly 90 % of total regenerated cellulosic fibers

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produced. Natural materials such as wood, bamboo, and cotton linters are the raw materials for this fiber. Viscose rayon is used as continuous filament and staple fibers, among which 90 % of viscose rayon is produced as staple fibers [1]. Since the twenty-first century, the production of viscose rayon has shifted from Europe, the United States, and other developed countries to the Asia–Pacific regions due to high labor costs and stringent environmental regulations. The developing countries in the Asia–Pacific regions are now producing about 80 % of the global viscose production with China being the world's largest viscose fiber producer accounting for about 62 % of the global total in 2012. The production of viscose fiber in China rose very quickly from 2006–2012 at an average compound annual growth rate of 12.1 %, leading to production of 2.588 million tons in 2012 [1]. Viscose fibers produced in China are mainly distributed in East, North, and Northwest China. However, China needs to import other types of high-end regenerated cellulosic fibers such as Lyocell and modal fiber. In 2012, the world's largest manufacturer of viscose fiber was Aditya Birla Group with production capacity of 800,000 tons and plants in countries including India, Thailand, Indonesia, and China. The second largest manufacturer was Austrian Lenzing, producing 770,000 tons (2011) in the plants located in Austria, Indonesia, China, the United Kingdom, and the United States. Besides holding the second rank in viscose fiber production, this company occupies a monopolistic position in Lyocell and modal fiber production. Other large viscose fiber producers are mainly from China. In 2012, 77.3 % of total viscose fiber in China was produced by the top 10 viscose fiber producers. Fulida Group and Xinxiang Chemical Fiber and Grace Group are the largest staple and filament fiber manufacturers in China, respectively. Jilin Chemical Fiber is the largest bamboo fiber company in China, producing 48,000 tons/year and 7,000 tons/year of staple and filament fibers in 2012, respectively [1]. This company is trying to maintain their dominant position in the bamboo fiber market through expansion of bamboo pulp and bamboo staple fiber production capacity [1].

2 Properties of Regenerated Cellulosic Fibers

2.1 Viscose Rayon Fiber

In 1891, English scientists Cross and Bevan discovered viscose rayon fiber. Viscose fiber was previously called artificial silk, wood-silk, or viscose silk and officially named viscose rayon by the National Retail Dry Goods Association in 1924. Longitudinal and cross-sectional views of viscose fiber are shown in Fig. 1.

Viscose fiber possesses excellent aesthetic properties like silk fiber, good feel, and drape characteristics. Viscose shows similar properties to those of cotton or other cellulosic fibers due to the presence of cellulose backbone in their structure. However, viscose possesses higher moisture absorbency as compared to cotton. Breathability, softness, comfort, and ease in dyeing with glowing colors are the other favorable properties of viscose fibers [4–7].

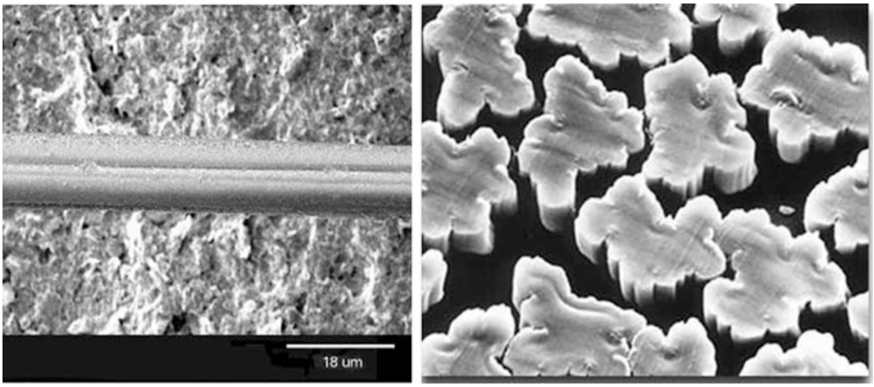


Fig. 1 Longitudinal and cross-sectional view of viscose fiber [2, 3]

Viscose rayon has good dry strength and abrasion resistance. However, it has poor resiliency and therefore, wrinkle formation is a problem. Its heat resistance is slightly less than that of cotton. To decrease cost or improve properties such as luster, softness, absorbency, and comfort, viscose is often used to blend with many other fibers.

The resistance of viscose rayon towards acids and alkalis is moderate and shows good resistance against bleaching agents and organic solvents. The burning characteristic of viscose fiber is similar to other cellulosic fibers [2, 5, 7, 8]. Physical properties of viscose fiber are listed in Table 1 and its chemical resistance is provided in Table 2.

2.2 Bamboo Viscose Fiber

Bamboo viscose fiber is produced from the cellulose obtained from the pulp of bamboo trees. Hebei Jiago Chemical Fiber Company in China grows most of the bamboo trees for production of bamboo viscose fiber. The Organic Crop Improvement Association (OCIA) has certified bamboo viscose fibers as organic fibers. Bamboo viscose is a 100 % cellulosic fiber obtained from natural resources and can degrade completely in soil through the action of microorganisms and sunshine, without causing any harmful effects to the environment. Figure 2 shows the cross-sectional and longitudinal views of the bamboo viscose fiber [9–14].

Bamboo viscose fiber possesses high breathability and coolness owing to the presence of numerous microlevel gaps and holes in its cross-section. This fiber presents good moisture absorption and ventilation properties [9, 11, 13]. The physical properties of bamboo viscose fiber are given in Table 3.

Table 1 Physical properties of viscose rayon [3]

Properties	Values
Tenacity (gram per denier)	
Dry	2.5–3.0
Wet	1.4–2.0
Breaking elongation (%)	
Dry	16–24
Wet	21–29
Recovery from stretch (2 %)	85 %, poor
Cross section	Serrated
Moisture regain (%)	11–14
Density (g/cc)	1.50

Table 2 Chemical properties of viscose rayon [3]

Chemical agents	Resistance
Acids	Damaged by strong acids and moderate effect with weak acids
Alkalis	Good resistance against weak alkalis but strong alkali is harmful
Bleaching agents	Strong oxidizing agents damage viscose rayon fiber
Organic solvents	Good
Mildew	Not good
Insects	Not good

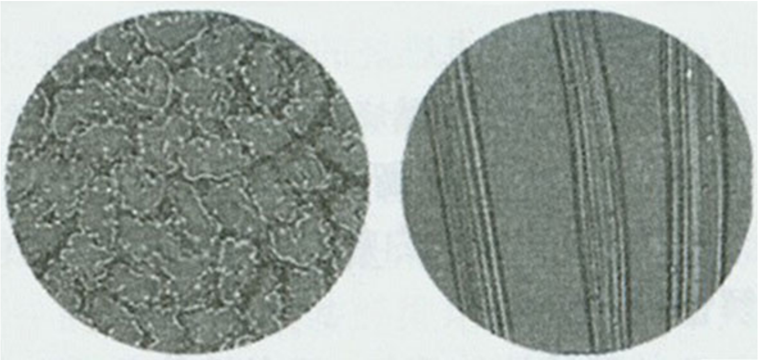


Fig. 2 Cross-sectional and longitudinal views of bamboo viscose fiber [13]

Table 3 Physical properties of bamboo viscose fiber [13]

Properties	Values
Tenacity (cN/tex)	
Dry	2.2–2.5
Wet	1.3–1.7
Dry breaking elongation (%)	14–18
Cross section	Serrated with microgaps and holes
Moisture absorbency rate %	90–120
Moisture regain (%)	13
Density (g/cc)	1.32

2.3 Cellulose Acetate Fiber

Cellulose acetate is one of oldest regenerated fibers produced from the cellulose derived from wood sources. Camille and Henry Dreyfus first developed the commercial process to produce cellulose acetate fiber in 1905 and the spinning of cellulose acetate fibers was commercialized in 1924 in the United States [15–17]. Over the other textile fibers, cellulose acetate presents some uncommon characteristics. This fiber possesses good luster and is softer than viscose and other textile fibers. Cellulose acetate has very good handle (soft, smooth, dry, crisp, and resilient) and comfort properties (breathes, wicks, dries quickly, and no static cling). Fabrics made from cellulose acetate also give very good handle characteristics and are easily dyeable to brilliant, soft, and attractive shades [15, 17, 19]. Figure 3 shows the longitudinal and cross-sectional views of cellulose acetate fiber and its physical properties are listed in Table 4. Table 5 presents the chemical properties of cellulose acetate fiber.

2.4 Cuprammonium Rayon Fiber

Cupromonium rayon is produced through regeneration of wood cellulose dissolved in a cuprammonium solution. To produce this fiber, cellulose is made soluble by combining it with copper and ammonia [20, 21]. The longitudinal and cross-sectional views of this fiber are shown in Fig. 4.

2.4.1 Properties of Cuprammonium Rayon

Cuprammonium fiber can be produced in extremely fine deniers (1.33 denier is produced regularly, whereas the common denier for viscose rayon is around 2.5) to obtain softness and handle characteristics similar to silk. The burning characteristics of this fiber are similar to viscose rayon; it burns rapidly and chars at 180 °C.

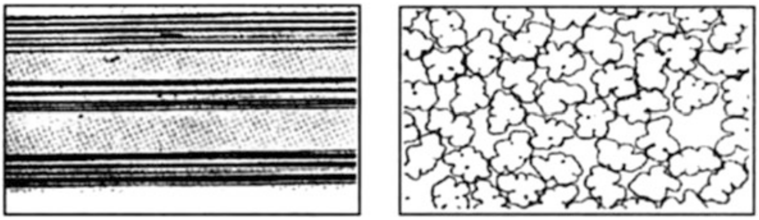


Fig. 3 Longitudinal and cross-sectional views of cellulose acetate fiber [18]

Table 4 Physical properties of cellulose acetate fiber [15]

Physical properties	Cellulose acetate
Tenacity (g/d))	0.9–1.4
Density (g/cc)	1.32
Elongation at break (%)	Very good
Elasticity	Not so good
Moisture regain (%)	6
Resiliency	Not good
Melting point	230 °C
Abrasion resistance	Moderate
Luster	Light to bright

Table 5 Chemical properties of cellulose acetate fiber [15]

Chemical/biological agents	Resistance
Acids	Soluble
Alkalis	Strong alkali damages and weak alkali also damages slightly
Bleaching agents	Strong oxidized agents will damage but it has strong resistance against weak oxidizing and reducing agents
Organic solvents	Soluble in acetone. Dry cleaning agents do not affect cellulose acetate
Mildew	Good
Insects	Good

Ashes produced from this fiber after ignition contain copper. Degradation and weakening occur due to exposure to sunlight in the presence of oxygen and moisture. Tensile strength of the fiber is in the range of 1.7–2.3 g/d in the dry state and 0.9–2.5 g/d in the wet state. The elongation at break in the dry state is 10–17 % and moisture regain at 70 °F and at 65 % RH is 11 %. The fiber has a round and smooth cross-section or occasionally slightly oval [23].

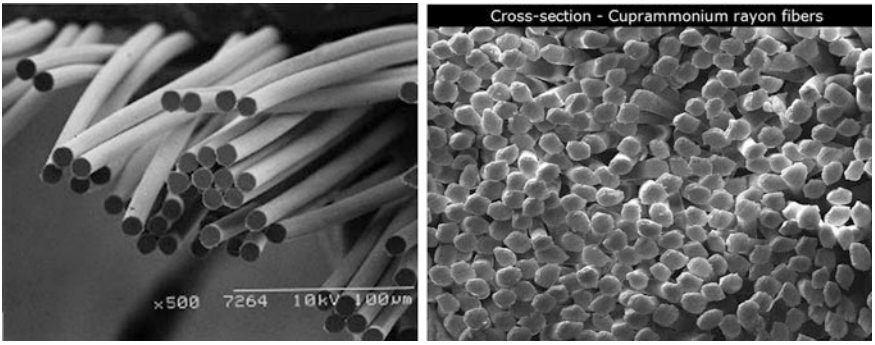


Fig. 4 Longitudinal and cross-section views of cuprammonium rayon fiber [22]

2.5 Lyocell Fiber

Lyocell (trade name, Tencel®) is the first new-generation cellulosic fiber spun using solvent spinning technology. The demand for an environmentally favorable process of producing fibers from renewable raw materials led to the development of Lyocell technology. This fiber was produced first in 1984 and on a commercial scale in 1988 [24–30].

Lyocell fiber is completely biodegradable. It possesses good moisture absorbency. Unlike viscose, Lyocell fiber presents high strength in both wet and dry conditions. This fiber can be easily blended with other fibers such as linen, wool, and cotton. Fibrillation of Lyocell fiber occurs when it is abraded in the wet state leading to formation of surface fibrils. These surface fibrils remain attached to the fibers, but peel away from the fiber surface producing an eye-catching aesthetic appearance. The longitudinal and cross-sectional views of Lyocell fiber are shown in Fig. 5.

The advantageous features of fabrics made from Lyocell fiber are wrinkle resistance (due to high modulus), good stability to washing, dyeability to vibrant colors with a variety of effects and textures, and good drapeability [24, 26]. The basic physical properties of Lyocell fibers are listed in Table 6 and compared with other textile fibers.

2.6 SeaCell Fiber

SeaCell fiber (see Fig. 6) is a third-generation regenerated cellulosic fiber. This fiber is produced using an innovative Lyocell technique, in which seaweed containing vitamins, minerals, and trace elements are added to the cellulose pulp before the spinning process. As a result, the produced fiber provides health-promoting and skincare effects. Commonly, SeaCell fibers are produced from cellulose either adding only seaweed (SeaCell® pure) or adding both seaweed and silver (SeaCell® active) [31, 32].

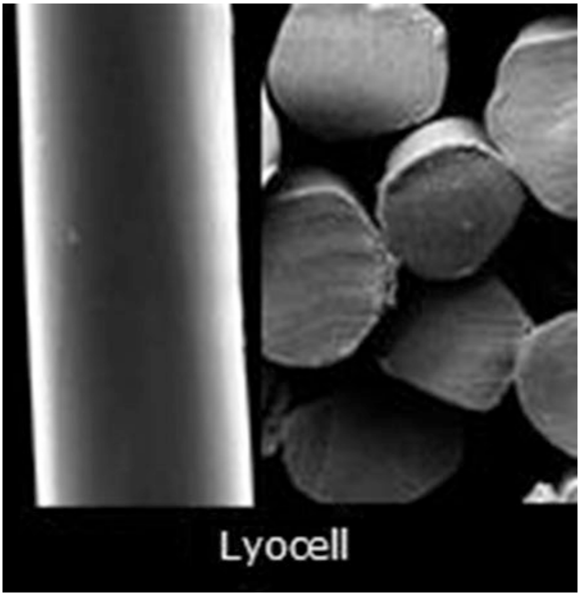


Fig. 5 Longitudinal and cross-sectional views of Lyocell fiber

Table 6 Physical properties of Lyocell fiber [24]

Property	Tencel	Viscose	Cotton	Polyester
Fiber fineness (dtex)	1.7	1.7	–	1.7
Dry tenacity (cN/tex)	38–42	22–26	20–24	55–60
Dry elongation (%)	14–16	20–25	7–9	25–30
Wet tenacity (cN/tex)	34–38	10–15	26–30	54–58
Wet elongation (%)	16–18	25–30	12–14	25–30

Fig. 6 Roving of Seacell fiber [33]

Seacell fiber possesses softness and breathability, providing a pleasant feeling of well-being. SeaCell® active is suitable for medical textiles due to its antibacterial and fungicidal properties. SeaCell fiber can be easily blended with synthetic and natural fibers and it is most suited for application in underwear and childcare textiles [31]. The physical properties of Seacell fiber are provided in Table 7.

2.7 Modal Fiber

Modal fiber is produced through regeneration of cellulose obtained from the pure wood pulp of beech trees. Unlike viscose rayon, which can be produced from the wood pulp of different trees, the wood pulp obtained from beech wood is the only source of cellulose for the production of modal fiber. Therefore, modal is a type of viscose rayon fiber. This fiber possesses high tenacity and high wet modulus [34, 35]. Figure 7 shows the longitudinal and cross-section views of modal fiber. Modal fiber has a higher wet modulus and lower elongation compared to viscose rayon due to its higher degree of polymerization. This fiber possesses a silk-like texture (luster, shine, and gloss) and smoother surface than mercerized cotton [37–39]. Physical properties of modal fiber are provided in Table 8 and compared with viscose rayon fiber.

3 Production Process of Regenerated Cellulosic Fibers

3.1 Production Process of Viscose Rayon

Cellulose extracted from some varieties of trees such as spruce, pine, and hemlock is the raw material for producing viscose rayon fiber. The manufacturing steps of viscose rayon fiber are as follows [5–8].

3.1.1 Cellulose Purification

First, cellulose extracted from trees is purified. For this purpose, the bark of spruce or other trees is removed and after cutting into small pieces treated with a solution of calcium bi-sulphite in steam under pressure for about 14 h. This treatment removes the lignin present in the wood by converting it into water-soluble sulphonated compounds, without affecting the cellulosic part of the wood. Purified cellulose is then obtained after washing with water and subsequently, purified cellulose is bleached using sodium hypochlorite. It is then converted into paper boards or sheets, known as wood pulp, which is usually purchased by the manufacturers for producing viscose rayon.

Table 7 Physical properties of Seacell fiber [31]

Properties	SeaCell fiber
Fiber fineness (dtex)	1.7
Strength (cN/tex)	≥35
Wet strength (cN/tex)	≥30
Elongation (%)	13
Dry elongation (%)	17
Wet modulus (cN/tex)	≥180

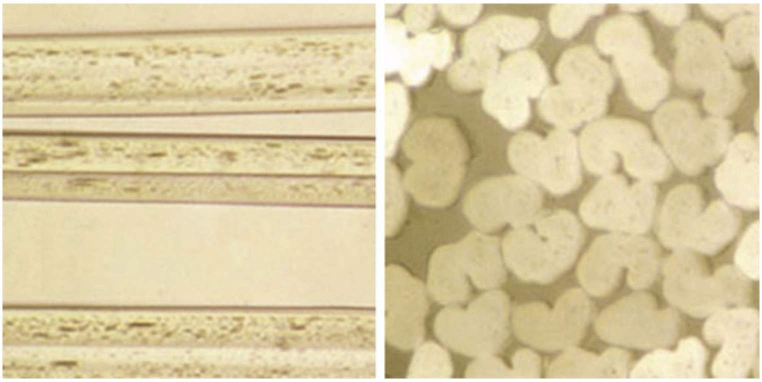


Fig. 7 Longitudinal and cross-section of modal fiber (1.3dtex) [36]

Table 8 Comparison of physical properties of modal and viscose rayon fiber [38]

Properties	Modal fiber	Viscose rayon
Fiber density (g/cm^3)	1.53	1.51
Tenacity (g/d)		
Dry	2.2–4.0	1.2–3.0
Wet	3.8–5.0	0.5–0.8
Breaking elongation (%)		
Dry	7.0	15–30
Wet	8.5	30
Moisture regain (%)	11.8	12.5

3.1.2 Conditioning of Wood Pulp

After purification, the desired moisture is added to the wood pulp by keeping it in a conditioning room with good air circulation and temperature maintained at 30 °C.

3.1.3 Steeping Process

The conditioned wood pulp is next subjected to the steeping process, that is, treated with 17.5 % caustic soda solution to convert cellulose into soda cellulose. The wood pulp sheets are allowed to soak for about 1–14 h until the color turns dark brown. The sheets are then pressed to remove excess NaOH solution. 310 kg of soda cellulose is obtained from 100 kg of sulphated pulp.

3.1.4 Cutting or Shredding Process

A shredding machine is then used to cut the wet and soft sheets of soda cellulose into small bits and subsequently break into fine crumbs during a time period of around 2–3 h.

3.1.5 Ageing Process

Soda cellulose is then subjected to the ageing process which decreases the degree of polymerization of soda cellulose from 1,000 to 300. This is done by storing the soda cellulose in small galvanized drums for about 48 h at 28 °C. The degree of polymerization decreases due to the oxygen present in the air contained in the drum.

3.1.6 Xanthation or Churning Process

Sodium cellulose xanthate is then formed by treating the soda cellulose crumbs with carbon disulphide (10 % by weight of the crumbs) in air-tight hexagonal mixers rotating at a speed of 2 rpm for 3 h. After this process, the colors of the product turn from white to reddish orange.

3.1.7 Mixing or Dissolving Process

Sodium cellulose xanthate is then mixed with caustic soda and stirred for 4–5 h in a dissolver. Cooling of the dissolver is also carried out. A clear brown thick liquor like honey is formed after dissolution of soda cellulose xanthate. This liquor, called viscose, contains about 6.5 % caustic soda and 7.5 % cellulose.

3.1.8 Ripening Process

In the ripening process, the viscose solution is stored for 4–5 days at 10–18 °C and this results in an initial decrease in viscosity and subsequent rise to the original value. The ripened viscose solution is then filtered carefully before spinning the filaments.

3.1.9 Spinning Process

The viscose solution is forced through the fine holes (diameter around 0.05–0.1 mm) of a spinneret immersed in a solution containing the following chemicals.

Sulfuric acid	10 %
Sodium sulphate	18 %
Zinc sulphate	1 %
Glucose	2 %
Water	69 %

The spinning solution temperature is maintained at 40–45 °C. The dissolved sodium cellulose xanthate precipitates out due to the presence of sodium sulphate in the coagulation bath and sulfuric acid converts the xanthate into cellulose, carbon disulphide, and sodium sulphate. The function of glucose present in the coagulation bath is to provide softness and pliability to the filaments whereas zinc sulphate is responsible for giving added strength. The manufacturing process of viscose rayon is presented in Fig. 8.

3.2 Production Process of Acetate Rayon

In the production of cellulose acetate [15, 17, 41], cellulose is treated with acetic acid to convert the free hydroxyl groups of cellulose into ester groups. This is then dissolved in acetone or chloroform and spun into fibers through evaporation of the solvent. Therefore, cellulose acetate is a regenerated as well as a modified cellulosic fiber unlike viscose and cuprammonium rayon which are pure regenerated cellulosic fibers.

3.2.1 Acetylation Process

Acetylation of purified cellulose pulp is carried out in a metal tank (acetylator) by treating it with a mixture of glacial acetic acid, acetic anhydride, and a small amount of concentrated sulfuric acid. 100 kg of cotton linters is treated with 300 kg of glacial acetic acid, 500 kg of acetic anhydride and 8–10 kg of concentrated sulfuric acid at 25–30 °C for 7–8 h by mixing thoroughly with the help of a stirrer with rotating blades. As the acetylation reaction is an exothermic reaction, it is favored by removing heat through circulation of cold water through a jacket surrounding the acetylator (see Fig. 9). The acetylation process leads to the formation of triacetate in the form of a suspension and is called the acid dope.

The acid dope is then stored in jars containing sulfuric acid, acetic acid, and water for 10–20 h to carry out the ripening process. This process partially converts the

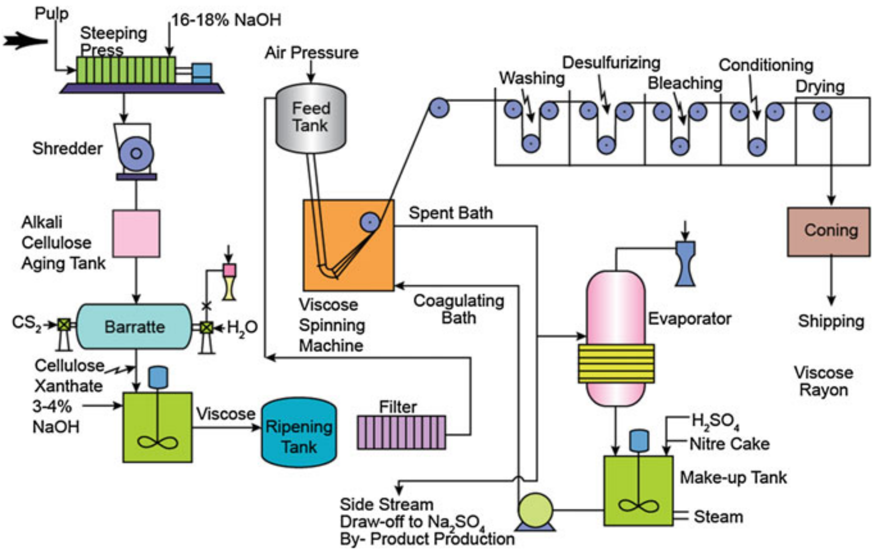


Fig. 8 Schematic diagram of the manufacturing process of viscose rayon fiber [40]

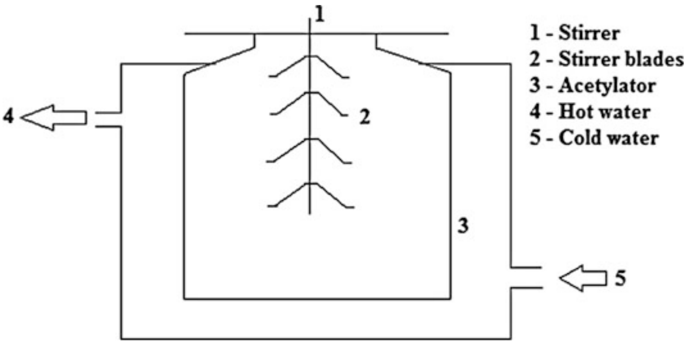


Fig. 9 Schematic diagram of acetylator [17]

acetate groups of cellulose acetate into hydroxyl groups. White flakes of cellulose acetate are then precipitated out as a result of water addition and continuous stirring. The cellulose acetate flakes are then dried after centrifuging the excess water.

3.2.2 Preparation of Spinning Solution

The dried acetate flakes are then slowly dissolved into acetone (ratio of cellulose acetate to acetone is 1:3) in enclosed tanks with the help of an intensive stirring process for 24 h. A thick clear dope is obtained and this is next filtered and deaerated.

3.2.3 Spinning Process

A dry spinning process is used to spin acetate rayon filaments. After the spinneret, the filaments are formed due to evaporation of solvents. The filaments travel a distance of 2–5 m vertically downwards to a feed roller and then pass over a guide roller to the bobbin at much higher speed than the spinning speed, in order to draw the filaments to some extent. The manufacturing process of cellulose acetate fiber is shown in Fig. 10.

3.3 Production Process of Cuprammonium Rayon

Similar to other cellulosic fibers, cotton linters are also the raw material for cuprammonium rayon [43]. Cotton linters are first purified using the following treatments: (a) mechanical treatment and (b) chemical treatment.

3.3.1 Mechanical Treatment of Cotton Linters

Mechanical treatment of cotton linters is carried out to open and remove the mechanically attached and loosely bound impurities such as dust, sand, seed residues, and so on.

3.3.2 Chemical Treatment of Cotton Linters

In the chemical treatment, Na_2CO_3 (soda ash) solution (2 %) and a small amount of dilute caustic soda are added to cotton linters and boiled under pressure for several hours. The fatty acids present in the cotton linters are converted to soluble substances due to reaction with soda ash and are removed.

3.3.3 Dissolution of Cellulose

In this process, 300–400 L of water is mixed with a solution of hydrated copper sulphate, a small amount of sugar, and caustic soda solution in a vessel at room temperature with stirring. Copper hydroxide is formed due to the reaction of copper sulphate and caustic soda. Copper cellulose is then formed through addition of ground cotton linters to the above mixture and filtered to remove the liquid. Copper cellulose is then dissolved in a solution of ammonia in water.

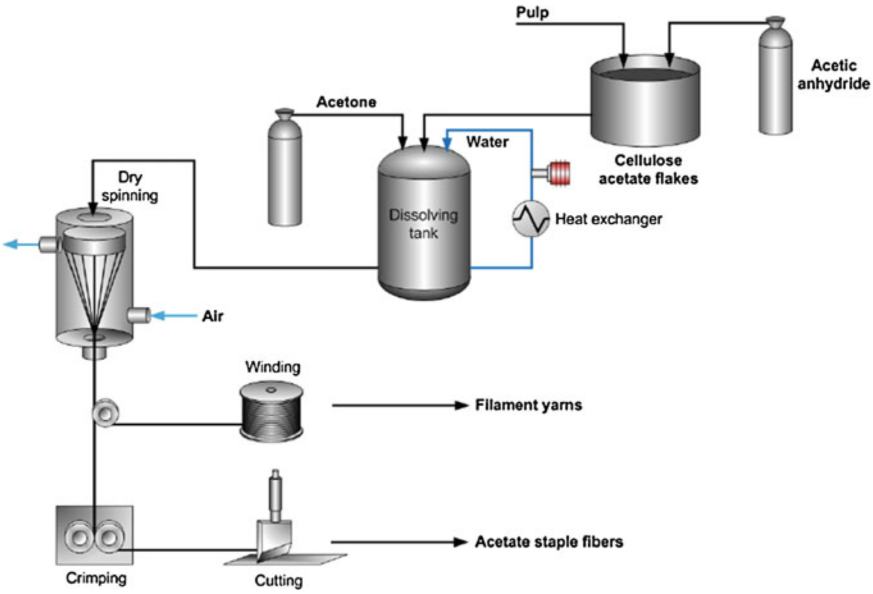


Fig. 10 Schematic diagram of acetate rayon manufacturing process [42]

3.3.4 Spinning Solution

To prepare a dope suitable for the spinning process, a few compounds are added to the cuprammonium solution such as glycerin, glucose, tartaric acid, citric acid, oxalic acid, cane sugar, and so on.

3.3.5 Wet Spinning

The spinning dope is discharged through the spinneret holes into the coagulation bath containing H_2SO_4 and this leads to formation of relatively thick filaments, which are subsequently stretched to reduce the fineness. Figure 11 shows the flowchart of the manufacturing process of cuprammonium rayon.

3.4 Production Process of Lyocell Fiber

In the Lyocell process, cellulose is dissolved in hot aqueous NMMO (N-Methylmorpholine-N-Oxide) solution due to the formation of hydrogen bonds between cellulose and polar NMMO. Subsequent addition of NMMO and removal of water results in a maximum cellulose concentration of about 23 %. The resulting solution is highly viscous, similar to lye (a liquid from wood ashes), and therefore this process and fibers produced are called Lyocell (i.e., lye of cellulose).

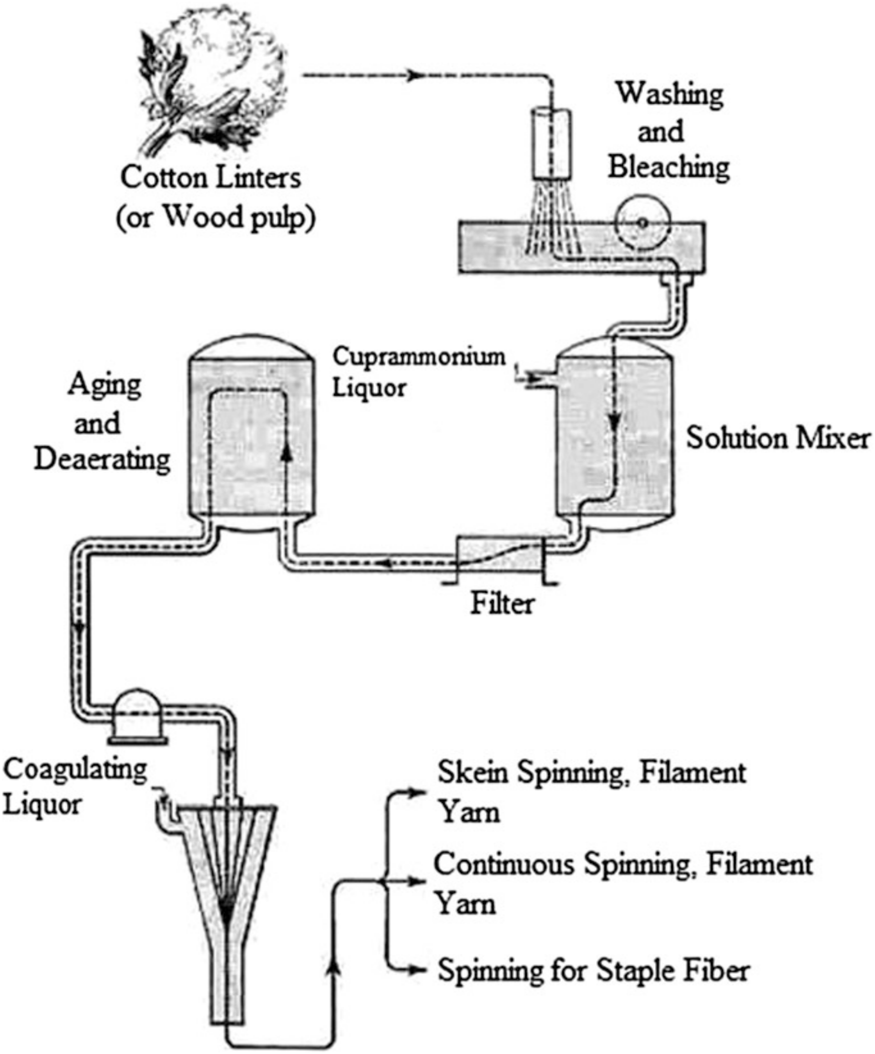


Fig. 11 Schematic diagram of manufacturing process of cuprammonium rayon fiber [44]

The spinning dope is extruded through a spinneret at high temperature which helps in easy extrusion through the decrease in viscosity of the spinning dope. Coagulation of extruded filaments is carried out in water. The produced fibers are then washed thoroughly to remove NMMO and dried. NMMO can be recovered up to 99.6 % after the spinning process. The Lyocell process allows the highest solvent recovery among all cellulosic fiber spinning processes [24–26]. The flowchart of Lyocell spinning process is provided in Fig. 12.

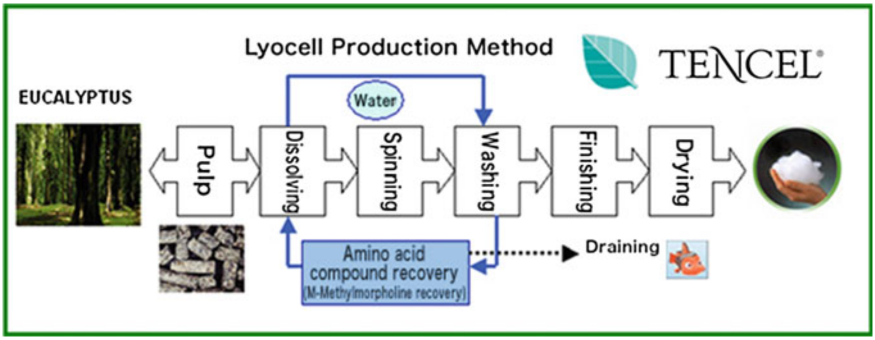


Fig. 12 Schematic diagram of the manufacturing process of Lyocell fiber [45]

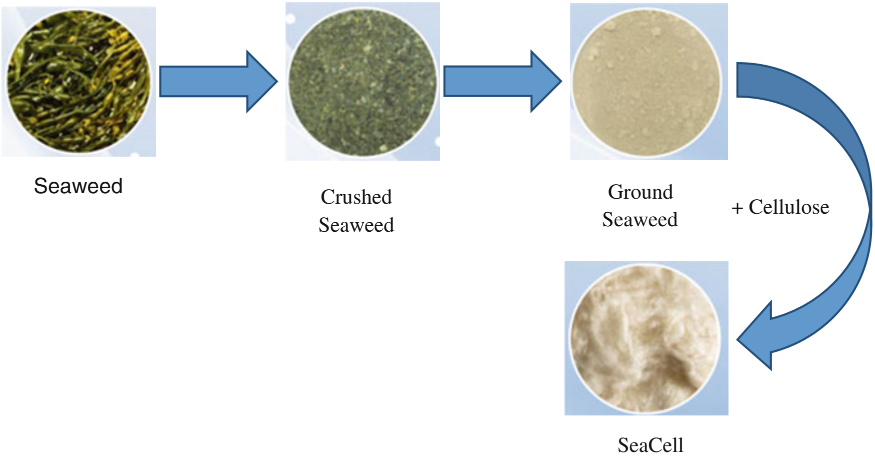


Fig. 13 Flowchart of seaweed extraction process for SeaCell fiber production [31]

3.5 Production Process of SeaCell Fiber

In the production of SeaCell fiber, cellulose pulp and seaweed are mixed together and spun into SeaCell fibers using the Lyocell production process [31]. Seaweed is extracted from the seaweed sources as follows (Fig. 13).

3.6 Production Process of Modal Fiber

Wet spinning is used to produce modal fibers. Due to the use of many chemicals in the spinning of modal fibers, this fiber can be called a biobased fiber instead of a natural fiber. Except for a few steps, the production process is similar to that of viscose rayon fiber [46].

3.6.1 Steeping and Pressing

In the steeping process, cellulose is converted to its alkoxide derivative (known as alkcell). For this purpose, cellulose pulp is treated with an aqueous solution of 17 % sodium hydroxide and this treatment results in the swelling of cellulose and conversion into sodium cellulosate. Then extra caustic soda is removed from the alkcell slurry by pressing.

3.6.2 Shredding

Alkcell contains 30–36 % cellulose and 13–17 % soda. Alkcell slurry is then opened through a shredding process, in order to facilitate the penetration of oxygen and CS_2 in the subsequent mercerizing and xanthation reactions.

3.6.3 Mercerizing or Ageing

After the shredding process, oxidative or irradiative depolymerization of cellulose is carried out in order to decrease the degree of polymerization.

3.6.4 Xanthation

The reaction of mercerized alkcell and CS_2 vapor is carried out under vacuum in order to form sodium cellulose xanthate. Sodium cellulose xanthate is then dissolved in a dilute NaOH solution to obtain the spinning dope.

3.6.5 Filtration and Deaeration

Before spinning, impurities present in the spinning solution are removed in order to prevent the choking of spinneret holes. The use of automatic mechanical filters of sintered metal screens with automatic backflush is a commonly used method. Subsequently, vacuum is applied to remove any dispersed air forming bubbles.

3.6.6 Spinning

In the modal fiber spinning, zinc is not used in the spinning bath as used in viscose rayon and coagulation is carried out in a cold low-acid–low-salt bath for only a short period. The process steps for wet spinning of modal fibers are shown in Fig. 14.

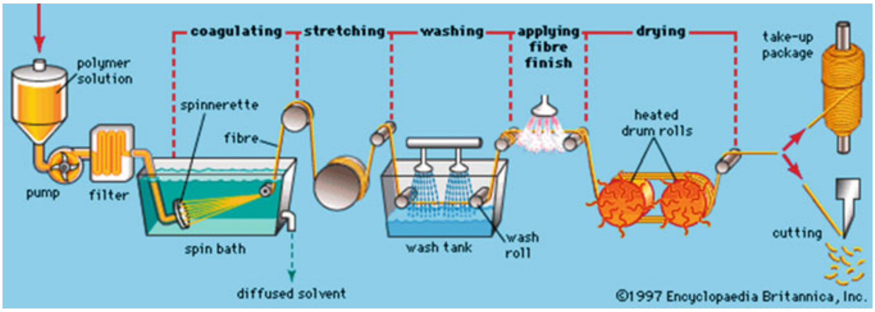


Fig. 14 Process steps for wet spinning process of modal fiber [47]

3.6.7 Coagulation

In the modal process, coagulation and stretching are done simultaneously before regeneration and this results in the formation of very high wet modulus fibers. Before regeneration, the filaments are drawn three times of their spun length leading to formation of a fibrillar fiber structure. The very high dry and wet modulus of modal fiber result from this stretching process which orients the cellulose molecules to a very high degree.

4 Impact of Production Process on Sustainability of Regenerated Cellulosic Fibers

4.1 Viscose Fiber

Viscose fiber is the first fiber developed in the family of regenerated cellulosic fiber. The important sustainability aspects of viscose fiber are as follows [48].

- The trees (such as pine, beech, etc.) from which the raw materials of viscose fiber are collected are replenishable. These trees usually grow using rainwater and therefore do not need any other type of water supply. Land used for these forests is specific and their use does not cause any environmental impact [48].
- Spinning of viscose fibers from wood pulp uses many chemicals, such as caustic soda, carbon disulphide (CS_2), sulfuric acid, sodium sulphate, and zinc sulphate. A high amount of caustic soda is used in the processing of viscose fiber and sodium sulphate is produced as a by-product. Nowadays, it possible to recycle and reuse up to 70 % of CS_2 and the remaining 30 % is converted into sulfuric acid which is also recycled by the process [48]. The main sustainability concern in the fiber production stage is the consumption of energy and the use of fossil fuel in fiber production as well as in the production of various chemicals including caustic soda, sulphur, and NaOCl. The lifecycle of viscose

Fig. 15 Lifecycle for viscose fiber [49]

fiber is shown in Fig. 15. The factors influencing the sustainability of cellulose acetate, cupramonium rayon, and modal fiber are more or less similar.

4.2 Bamboo Viscose Fiber

Bamboo viscose is regenerated fiber produced from the cellulose of bamboo trees through the viscose production process. The production of bamboo viscose is considered to be sustainable [50] because:

- No pesticides or chemical fertilizers are required for the growth of bamboo trees.
- Bamboo trees grow using rainwater and irrigation is not necessary.
- Replanting of bamboo trees is seldom required.
- The growth of bamboo trees is fast and harvesting can be done in 3–5 years.
- Oxygen production in the case of bamboo trees is 35 % more as compared to an equivalent stand of trees.

- Bamboo trees are therefore very important in terms of balancing oxygen and carbon dioxide in the atmosphere.
- Bamboo trees can provide very good protection against soil erosion.

The production of bamboo viscose is mostly a closed-loop system, in which NaOH used in the spinning process is recycled completely and also 74 % of CS_2 is recovered and recycled for further use. The use of caustic soda is approved for use in textiles under the GOTS as this chemical does not cause any harm if used and disposed of properly.

4.3 Lyocell Fiber

Significant environmental benefits and sustainability are the important advantages of Lyocell fibers [24]. The reasons behind the sustainability of Lyocell fiber are:

- Lyocell fiber is produced using raw material which is renewable. The trees from which the cellulose pulp is extracted are always replenished.
- Complete recycling of solvents (with very little loss) used in the production process of Lyocell fiber.
- Lyocell fiber is biodegradable.

The simplified lifecycle of Lyocell fibers, from the raw material to product disposal stage is shown in Fig. 16.

- Raw material for fiber production is wood pulp, extracted from trees grown in managed forests; that is, a reforestation process will be carried out after the deforestation.
- A very simple production step in which wood pulp is dissolved directly in a solvent (NMMO) and formed into fibers. Solvent is recovered almost completely (99.96 %.) and there are no chemical by-products.
- Lyocell fibers find widespread textile and industrial applications with significant environmental benefits during product manufacturing and use.
- At the end of the lifecycle, Lyocell fiber products are biodegradable and the biodegradation process contributes to photosynthesis and hence to the growth of new trees for future Lyocell production [24].

4.4 SeaCell Fiber

Some important sustainability aspects of Seacell fiber are:

- The raw material is wood pulp that comes from recycled or waste wood, and seaweed extracted from marine environments causing no harmful effects to the wildlife.

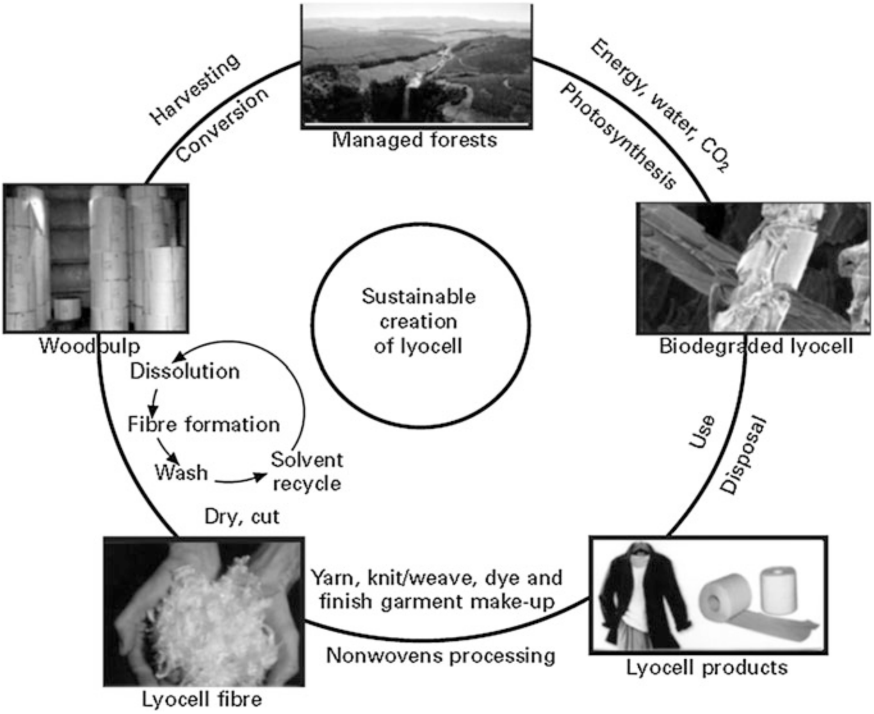


Fig. 16 Lyocell sustainability [24]

- It is biodegradable fiber.
- This fiber has good prospects for application in underwear or gym clothes due to its breathability and capability to pass nutrients into the skin [51].

5 Applications of Regenerated Cellulosic Fibers

5.1 Applications of Viscose Fiber

Apparel: Accessories, blouses, dresses, jackets, lingerie, linings, millinery, slacks, sport shirts, sportswear, suits, ties, work clothes [5–8].

Home Furnishings: Bedspreads, blankets, curtains, draperies, sheets, slipcovers, tablecloths, upholstery.

Industrial Uses: Industrial products, medical surgical products, nonwoven products, tire cord.

Other Uses: Feminine hygiene products.

5.2 *Application of Bamboo Viscose*

Bamboo intimate apparel: Used in sweaters, bathing suits, mats, blankets, and towels due to comfortable hand, special luster, bright colors, and good water absorbance. Due to antibacterial activities, it is used in underwear, tights, T-shirts, and socks. Owing to its antiultraviolet nature, it is used in summer clothing, especially for the protection of pregnant ladies and young children from the damages of ultraviolet radiation [11, 13].

Bamboo nonwoven fabric: It is used in the field of hygiene materials such as sanitary napkins, masks, mattresses, and food packing bags due to its antibacterial nature.

Bamboo sanitary materials: Used in sanitary materials such as sanitary towels, gauze masks, absorbent pads, bandages, surgical clothes, nurse's wear, and so on, due to its natural effect of sterilization and bacteria stasis.

Bamboo bathroom series: Due to good moisture absorption, soft feel, splendid colors as well as antibacterial characteristics, it is used in towels and bathrobes.

Bamboo decorating series: Used in wallpapers and curtains that can absorb ultraviolet radiation in various wavelengths, resulting in less harm to the human body. Also used in television covers, sofa slipcovers, and so on.

5.3 *Applications of Acetate Fiber*

- Used to produce different types of clothing such as women's night wear and formal wear, coats, accessories for Japanese dresses, blouses, sweaters, scarves, and so on [15, 17].
- Used to produce home furnishing and bedding products such as blankets, bed clothes, fabrics for curtains, and so on.
- Used for making umbrella fabrics and cigarette filters.

5.4 *Applications of Cuprammonium Rayon Fiber*

- For clothing [37].
  A variety of fabrics for women's wear, blouses, underwear, Japanese dresses, linings, accessories for Japanese dresses, scarves, and so on.
- For home furnishings and bedding.
  Curtain, bedclothes, cover cloths for mats, and so on.
- For other uses.
  Square cloth for wrapping things, umbrellas, and so on.

5.5 Applications of Lyocell Fiber

- Used to produce home textile products. The fiber is used in sleeping products such as mattresses, mattress pads, bed covers, and linens. It is also used to make botanic beds [24–26].
- Staple fibers are used to produce a variety of apparel such as denim, chino, underwear, casual wear, and towels.
- Filament fibers are used in items with silk-like appearance such as women's clothing and men's dress shirts.
- Used in conveyor belts, specialty papers, and medical dressings.

5.6 Applications of Seacell Fiber

- In blends with other fibers, Seacell fiber is used as knitted, woven, or nonwoven fabrics with excellent softness and breathability in sportswear and yoga attire as well as in sheets, towels, blankets, and baby clothing [31].
- Used by various activewear manufactures such as Lululemon, Orca triathlete outfitters, Adea yoga clothing and sleepwear, and Falke socks and hosiery.

5.7 Applications of Modal Fiber

Modal fiber is widely used in clothing as a replacement for cotton and may also be used in blends with cotton, wool, and other synthetic fibers such as spandex, and the like [52].

- Used for both clothing and household textiles.
- Used for tablecloths and bedding, bathrobes, upholstery, and in home furnishings. Also used in outerwear, sportswear, and leisurewear.
- Applications in undergarments and toweling purposes.
- Lenzing modal is used exclusively for soft flowing tops and lingerie; exclusively in knitwear markets having high-end apparel/nonapparel products.
- For socks and stockings, as well as in technical applications, such as tire cord, abrasive ground fabric, rubber cloths, and other coat supports.

6 Sustainability Studies on Regenerated Cellulosic Fibers: Environmental Impact Assessment

A few studies have been conducted to investigate the impacts of regenerated cellulosic fibers on sustainability. The environmental impact of these fibers has been assessed using the lifecycle assessment (LCA) tool. In one of these important studies, regenerated cellulosic fibers produced from Lenzing AG, which accounts for 1/5th of world's total regenerated cellulosic fiber production, were studied using LCA, and the environmental impact of these fibers has been compared with those of commonly used natural and synthetic fibers [53, 54]. All steps starting from the extraction of raw materials and fuels, followed by all conversion steps until the delivery of the staple fiber to the factory gate were considered. The details of fiber used for this LCA study are provided in Table 9.

6.1 Sustainability Parameters

The various sustainability factors considered were the use of energy, land, and water and CML impact factors such as global warming potential, abiotic depletion, ozone layer depletion, human toxicity, freshwater aquatic ecotoxicity and terrestrial ecotoxicity, acidification, photochemical oxidant formation, and eutrophication. To assess energy use, cumulative energy demand (CED), nonrenewable energy use (NREU), and renewable energy use (REU) were considered. CED is the cradle-to-factory gate primary energy, that is, energy found in its original or natural form, and is the sum of NREU (total of fossil fuel such as oil/gas/coal and nuclear energy from uranium) and REU (biomass, solar, hydro, and wind energy). In land use, only biomass production (agricultural and forest) was considered and other forms of land use such as for infrastructure (for fiber plant or a spinning factory) and transportation were not considered [56–58].

In the case of water use, the sum of original natural freshwater consumption in the form of process water, cooling water, and irrigation water was considered. These three types of water can have different energy requirements and environmental impacts. In the environmental impact categories, global warming potential (GWP), abiotic depletion, ozone layer depletion, human toxicity, freshwater aquatic ecotoxicity, terrestrial ecotoxicity, photochemical oxidant formation, acidification, and eutrophication were studied. The results obtained from this study were also normalized to determine the relative contribution of the impact of the selected product systems to the total environmental loads of that region in a one-year time period [59–62].

Table 9 Types and geographic scope of regenerated cellulose, cotton, PET, and PP fibers used in the LCA study [55]

Regenerated Cellulose Fiber

Fibers used	Trade Name (Fiber type)	Wood	Pulp	Fiber plant	Process energy
Viscose (Asia)	Lenzing viscose	Eucalyptus	Market pulp	Asia	Local electricity, coal, gas, oil
Viscose (Austria)	Lenzing viscose	European Beech	Integrated pulp and fiber production in Austria		Biomass, recovered energy from MSWI
Modal	Modal (modal)				
Tencel	Tencel (Lyocell)	Eucalyptus and Beech	Mixed Lenzing pulp and market pulp	Austria	70 % gas, 30 % biomass
Tencel (2012)	Tencel (Lyocell)				100 % recovered energy from MSWI

Commodity Fibers

Fibers used	Type	Geographic scope	Data source
Cotton	Natural fiber	US and CN	Literature data
PET	Polyester	Western Europe	
PP	Polyolefin	Western Europe	

6.1.1 Energy, Water, and Land Use

Energy requirements of the studied fibers are presented in Fig. 17. It can be noticed that NREU of all cellulose-based fibers is lower than PET and PP fibers. The lowest NREU can be observed in the case of viscose (Austria), whereas PET presented the highest NREU. Among the cellulosic fibers, viscose (Asia) showed 70 % more energy requirement than cotton, and Tencel also had a slightly higher NREU. On the contrary, modal, Tencel (2012), and viscose (Austria) required 30, 40, and 50 % less energy as compared to cotton, respectively.

Viscose (Asia) required relatively higher NREU as compared to cotton and regenerated cellulosic fibers due to the use of relatively inefficient coal-based heat and power production (Fig. 18). Fossil fuel use in fiber production was the most important factor influencing the energy requirements of various fibers. However, energy use in the production of chemicals used in the manufacturing process of regenerated cellulosic fibers was also an important factor. In the case of viscose (Austria) and modal, the process energy from fossil fuels did not have such a significant influence unlike the energy required for caustic soda production which accounted for more than half of the NREU (Fig. 18). Production of other chemicals such as sulphur, CS_2, and NaOCl (sodium hypochlorite) also had a significant contribution to energy use. The Lyocell process, however, involves a much lower use of chemicals as compared to viscose rayon. The use of natural gas contributed

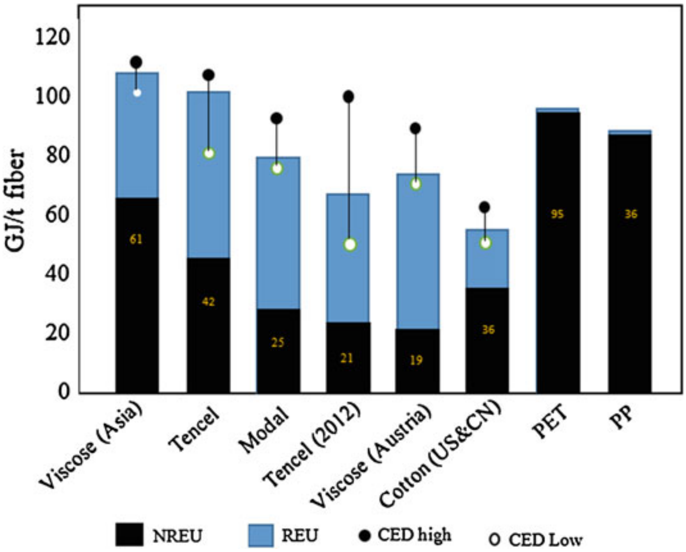


Fig. 17 Cradle-to-factory gate primary energy requirements (NREU, REU, and CED) of one tonne of staple fiber (default allocation method for by-products) [55]

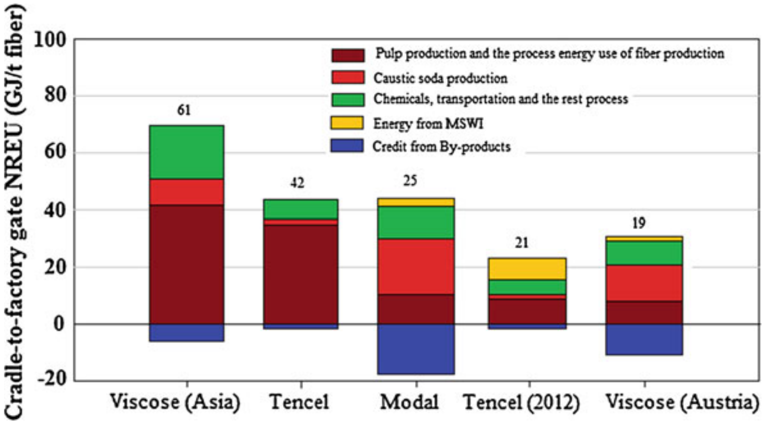


Fig. 18 Breakdown of cradle-to-factory gate NREU of regenerated cellulosic fibers (default allocation methods for by-products) [55]

more than 70 % of the total NREU of current Tencel fiber. However, the NREU of Tencel (2012) decreased by half (from 42 to 21 GJ/t) because the energy recovered from external municipal solid waste incineration (MSWI) was used to supply the process energy (Fig. 18). It can also be noticed that the REU for the regenerated cellulosic fibers was significantly higher than that of cotton, PET, and PP owing to the use of renewable feedstock and also due to the use of a large amount of biomass energy in the production.

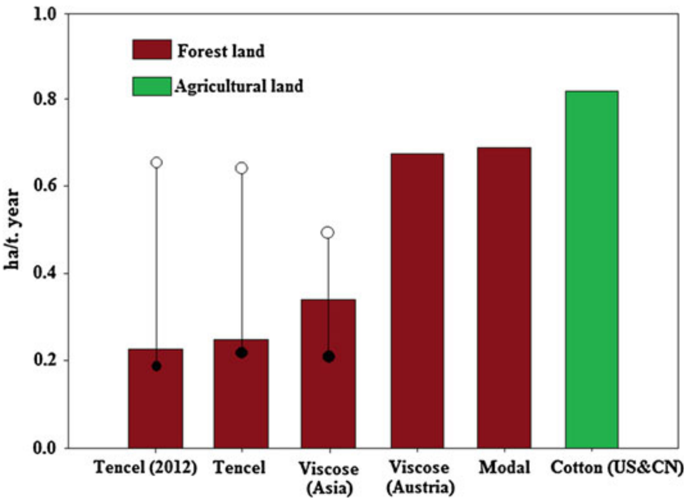


Fig. 19 Land use for biomass production for one tonne of staple fiber (economic allocation for by-products) [55]

Table 10 Water use for one tonne of staple fiber, based on natural water origin (m^3 per tonne of fiber, default allocation method for by-products) [55]

Type	Fiber	Process water	Cooling water	Irrigation water
Petrochemical fiber	PP (W. Europe)	<2	74	–
	PET (W. Europe)	<5	125	–
Regenerated cellulosic fiber	Viscose (Asia)	11	308	–
	Tencel (2012)	20	243	–
	Tencel	20	243	–
	Viscose (Austria)	42	403	–
	Modal	43	429	–
Cotton	Cotton (US and CN)	<5	37	5690 (4300–6860)[a]

[a] The lower range represents average US cotton; the higher range represents average Chinese cotton

It can be observed from Fig. 19 that the land requirement for cellulose fibers produced based on European wood was higher than those produced based on eucalyptus wood grown in warmer regions. This was because the forestry biomass yields in Europe are much lower than those of warmer regions. As MSWI was used as the source of process heat in the case of Tencel (2012) instead of biomass, the land use for this fiber was lower than Tencel fiber. However, among the studied fibers, cotton showed the maximum land use, mainly agricultural land.

It is clear from Table 10 that 90–90 % of the total water used in the case of cellulosic fibers is the cooling water. Processed water which includes softened water, deionized water, decarbonized water, and tapwater accounts for the rest, 5–10 %. It is interesting to note that water use in the case of cotton is significantly higher than that of regenerated cellulosic fibers; excluding cooling water, 100–500 times more water is consumed in the case of cotton and including cooling water, the consumption is about 10–20 times higher. Water is used mainly for the irrigation of cotton and for the average Chinese and US cotton, groundwater supplies about 70 % of the irrigation water and the rest (30 %) is supplied by surface water. Among the different forms of water use, irrigation water has strong environmental impacts as it may lead to freshwater resource depletion, soil salination, and water shortage downstream of the river.

6.1.2 Global Warming Potential

It can be seen from Fig. 20 that all regenerated cellulosic fibers have lower global warming potential as compared to polyester fibers. Except for viscose (Asia), other regenerated cellulosic fibers have very low GWP, nearly zero for modal and Tencel (2012), and negative for viscose (Austria). The negative GWP in case of viscose (Austria) indicates that it takes more carbon dioxide from the environment than it emits. The contribution of the process to the GWP for one tonne of regenerated cellulosic fibers is shown in Fig. 21.

For viscose (Asia), the factors responsible for its total carbon emissions are the market pulp, process heat, and power used in fiber production and also production of caustic soda and other chemicals, whereas for viscose (Austria) and modal, production of caustic soda is the most important factor and is responsible for more than 50 % of the total fossil carbon emissions. The avoided fossil carbon emissions from the by-products (especially Na_2SO_4 and acetic acid) are the primary reason for low GWP in the case of modal fiber. In the case of Tencel, combustion of natural gas for process heat accounts for more than 50 % of fossil carbon emissions. The use of an alternative energy source in the case of Tencel (2012) results in 90 % lower GWP as compared to Tencel which uses natural gas.

6.1.3 Abiotic Depletion

According to Table 11, among the regenerated cellulosic fibers, the highest impact on abiotic depletion is shown by viscose (Asia), whereas Tencel (2012) shows the lowest impact. The impact of the synthetic fibers, PET and PP, are higher than cotton and regenerated cellulosic fibers. Coal, market pulp, and caustic soda account for nearly 60 % of the abiotic depletion impact. More generally, for the fibers produced with the viscose process, caustic soda, CS_2, and sulphur production are the most important factors next to process energy use. For fibers based on the Lyocell process (i.e., Tencel), the process energy and market pulp are the most important factors, whereas the material consumption plays a less key role.

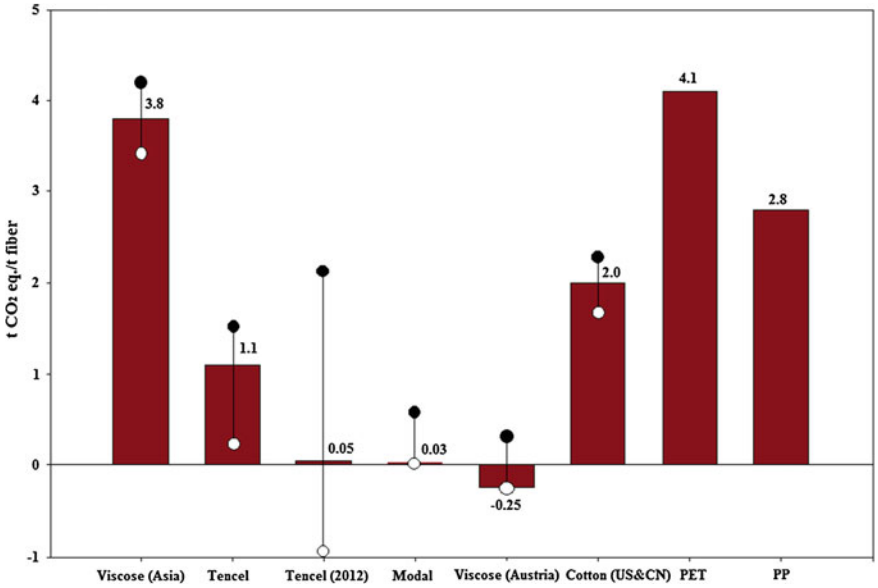


Fig. 20 Cradle-to-factory gate GWP for one tonne of staple fiber [55]

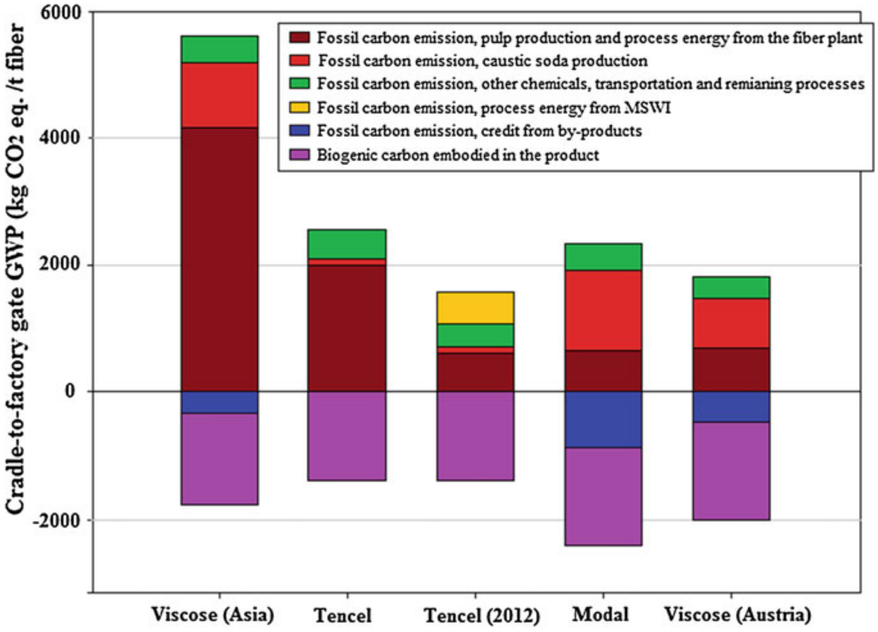


Fig. 21 Process contribution to cradle-to-factory gate GWP for one tonne of manmade cellulose fibers [55]

Table 11 Cradle-to-Factory Gate Environment Impact Assessment of One Tonne of Staple Fiber [55]

	Cotton	PET	PP	Viscose (Asia)	Viscose (Austria)	Modal	Tencel	Tencel (2012)
Abiotic depletion (kg Sb eq./t)	17	45	42	40	14	18	20	7
Ozone layer depletion ($\times 10^{-4}$ kg CFC11 eq.t)	2.0	0.7	0.7	2.8	0.3	0.4	1.1	0.7
Human toxicity (kg 1,4 DB eq./t)	1,700	4,393	369	1,490	630	765	470	660
Freshwater aquatic ecotoxicity (kg 1,4 DB eq./t)	17,310	58	53	160	74	93	85	75
Terrestrial ecotoxicity (kg 1,4 DB eq./t)	1,568	12	12	16	11	16	5.0	5.0
Photochemical oxidant formation (kg C_2H_4 eq./t)	0.7	1.0	0.6	1.8	0.5	0.5	0.6	0.4
Acidification (kg SO_2 eq./t)	41	21	11	45	14	15	17	13
Eutrophication (kg $PO_4{}^{3-}$ eq./t)	22	1.2	1.0	2.3	1.2	1.3	1.8	1.9

6.1.4 Ozone Layer Depletion

Processes that require oil as input show a relatively high ozone layer depletion impact because of Halon emissions from crude oil production. Halon is used in fire extinguishing systems, especially in the Middle East, Russia, and Africa. Viscose (Asia) has the highest impact on ozone layer depletion of all fibers studied. Approximately 95 % of the impact of viscose (Asia) is related to oil consumption for transportation, process fuels, and the production of grid electricity [63].

6.1.5 Human Toxicity, Freshwater Aquatic Ecotoxicity, and Terrestrial Ecotoxicity

For the human toxicity of viscose fibers, the most important processes are the production of caustic soda, market pulp, and external electricity use. These three factors account for more than 70 % of the total human toxicity impact of viscose (Asia). These factors cause little or no impact for the Tencel fibers. Tencel (2012) has a slightly higher human toxicity than Tencel because of emissions from the waste incineration plant. For cellulose fibers, pulp and caustic soda production are the most important factors for freshwater ecotoxicity and terrestrial ecotoxicity. For all cellulose fibers studied, the credits related to by-products, especially Na_2SO_4 and acetic acid, significantly contribute to lower human toxicity impacts and freshwater aquatic ecotoxicity. Terrestrial ecotoxicity is not particularly influenced by the credits of the by-products.

6.1.6 Photochemical Oxidant Formation

SO_2 emission is the main factor responsible for photochemical oxidant formation in the case of regenerated cellulosic fibers. The main causes of SO_2 emission is the use of SO_2 in the pulp production process and SO_2 emissions from energy production. The highest photochemical oxidant formation is observed in case of viscose (Asia) due to high SO_2 emissions during energy production in the fiber plant.

6.1.7 Acidification

Similar to photochemical oxidant formation, SO_2 emissions are mainly responsible for acidification. Among the regenerated cellulosic fibers, viscose (Asia) presents the highest emissions of SO_2 and impact on acidification, which is comparable to cotton fiber. The impacts of viscose (Austria), modal, Tencel, and Tencel (2012) on acidification are relatively lower and mainly caused due to the production of SO_2 in the pulp mill.

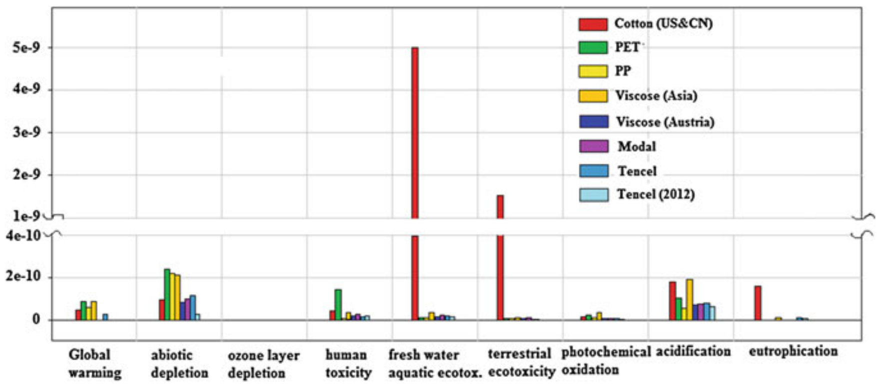


Fig. 22 Comparison of cradle-to-factory gate environmental impacts for one tonne of staple fiber normalized to World 2000 [55]

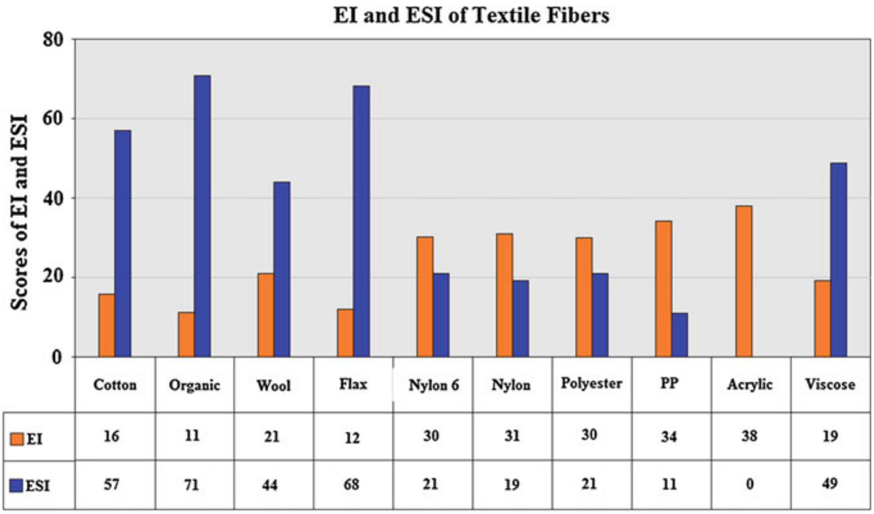
6.1.8 Eutrophication

Production of pulp and caustic soda are the important processes responsible for eutrophication in the case of regenerated cellulosic fibers, contributing about 50 % of the total impact for viscose (Asia). Another important factor contributing to eutrophication is the NOx emissions. Tencel (2012) has a significant contribution to eutrophication, resulting from the energy recovered from MSWI.

6.1.9 Normalized Environmental Impacts

The normalized environmental impacts of different fibers are represented in Fig. 22. It can be noticed that these fibers do not present visible effects on ozone layer depletion and photochemical oxidant formation. Also, the effects of regenerated cellulosic fibers on human toxicity, freshwater aquatic ecotoxicity, and eutrophication are not so significant. It is also evident that viscose (Austria) and Tencel (2012) do not make a significant contribution to the studied environmental impact categories. However, global warming, abiotic depletion, and acidification are the important environmental impact categories to be considered for viscose (Asia) fibers. In case of modal and Tencel, abiotic depletion and acidification can be considered as the relatively important environmental issues.

In a study conducted by Muthu et al. [64], sustainability of various textile fibers including viscose rayon was compared. In this study, the amount of energy and water consumed and greenhouse gases emitted were considered in a lifecycle inventory (LCI), and a lifecycle impact assessment (LCIA) was performed to evaluate the impact categories causing harmful effects to human health and related to ecosystem quality and resources. These factors which mainly influence the ecological sustainability were then used to establish a scoring system that was subsequently used to



	Cotton	Organic	Wool	Flax	Nylon 6	Nylon	Polyester	PP	Acrylic	Viscose
🟧 EI	16	11	21	12	30	31	30	34	38	19
🟦 ESI	57	71	44	68	21	19	21	11	0	49

Fig. 23 EI and ESI values of textile fibers

derive the environmental impact index (EI). Also, an ecological sustainability index (ESI) was determined from the EI values of different fibers.

The estimated EI and ESI values for different fibers are presented in Fig. 23. It can be observed that the EI of viscose fibers is lower than the petrochemical-based fibers such as nylon, polyester, PP, and acrylic and, consequently, ESI of viscose is better than these fibers. However, the environmental impact of viscose is higher than natural fibers such as cotton (both conventional and organic), wool, and flax fibers. Among these fibers, the highest impact is observed in the case of acrylic, whereas organic cotton fiber shows the lowest impact and highest ESI. Flax fiber needs the lowest amount of energy among all the studied fibers and consumes less water than cotton, leading to very low EI and high ESI values. In the case of organic cotton, no use of synthetic pesticides and fertilizers results in the lowest environmental impact and highest ecological sustainability. The reasons for the higher impact of viscose than other natural fibers, in spite of using less water than conventional cotton, are more damage to human health (due to the use of many chemicals in the viscose production process) and ecosystem quality, use of more resources during the production process, and lower capacity to absorb CO_2 than that of plants.

In another study, NREU and greenhouse gas (GHG) emissions of regenerated cellulosic fibers were compared with petrochemical PET, biobased PET, PLA, recycled PET, and recycled biobased PET [65]. As also observed in other studies, GHG emissions are highest for petrochemical PET. The lowest GHG emissions among all fibers studied were observed in the case of man-made cellulose fibers produced in integrated plants. Among the regenerated cellulosic fibers, modal and Tencel fibers show lower NREU and GHG emissions as compared to viscose fibers.

7 Conclusions

This chapter discusses various regenerated cellulosic fibers, mainly their production, properties, applications, and sustainability issues. Viscose rayon is one of the most widely used regenerated cellulosic fiber and very popular due to its aesthetic properties like silk fiber, and good feel and drape characteristics. Viscose fiber is extensively used in apparel, home furnishings, and industrial applications. Viscose fiber is produced from renewable resources (trees such as pine, beech, etc.), which grow using rainwater and, the land used for these forests is specific and therefore the growth of these trees does not cause any significant environmental effects. However, the one important sustainability factor for this fiber is the use of many chemicals, such as caustic soda, carbon disulphide (CS_2), sulfuric acid, sodium sulphate, and zinc sulphate during their spinning process. However, nowadays, this problem has been minimized through the recycling and reuse of up to 70 % of CS_2 and conversion of the remaining 30 % to sulfuric acid which is also recycled to the process. The main sustainability concern existing today for viscose rayon fiber is the consumption of energy and the use of fossil fuel in fiber production as well as in the production of various chemicals including caustic soda, sulphur, and NaOCl. Bamboo viscose fiber is a type of regenerated cellulosic fiber produced using the wood pulp of bamboo trees through the viscose rayon production process. Cultivation of bamboo trees are sustainable as bamboo is grown without pesticides or chemical fertilizers, requires no irrigation, rarely needs replanting, grows rapidly and can be harvested in 3–5 years, produces 35 % more oxygen than an equivalent stand of trees balancing oxygen and carbon dioxide in the atmosphere, and acts as an excellent soil erosion inhibitor. However, due to a similar production process to viscose rayon, the production of bamboo viscose also involves similar factors influencing its sustainability. Production of other regenerated fibers such as modal, cupramonium rayon, and cellulose acetate also involves many chemical reaction steps and the use of many chemicals, and the factors affecting their sustainability are also similar. Cellulose acetate is a regenerated as well as modified cellulosic fiber unlike viscose, modal, and cuprammonium rayons which are pure regenerated cellulosic fibers. Cellulose acetate fiber presents very good handle (soft, smooth, dry, crisp, and resilient) and comfort properties (breathes, wicks, dries quickly, and no static cling) and finds widespread applications in different types of clothes such as women's nightwear and formalwear, coats, accessories for Japanese dresses, blouses, sweaters, scarves, and the like, and also in home furnishings and bedding products such as blankets, bedclothes, fabrics for curtains, and so on. Cupramonium rayon fiber can be spun in extremely fine denier and possesses softness and handle characteristics similar to silk fiber. This fiber is used in similar applications to those of cellulose acetate fibers. Modal is produced through regeneration of cellulose obtained from the pure wood pulp of beech trees. Modal fiber has high modulus in both dry and wet conditions and possesses silk-like texture (luster, shine, and gloss) and a smoother surface than mercerized cotton. This fiber finds applications in clothing, home furnishings, undergarments, and socks and stockings, among others. Among the various regenerated cellulosic fibers, Lyocell fiber presents significant environmental benefits. In addition to being produced from renewable resources and completely biodegradable, Lyocell fiber is produced using a solvent that can be recovered almost completely. LCA studies carried out on these fibers showed that Lyocell fiber production (especially based on the use of MSWI as the source of process energy) is advantageous over the other regenerated cellulosic fibers due to lower requirements of energy, water, and land as well as lower impacts on global warming potential, abiotic depletion, ozone layer depletion, human toxicity, freshwater aquatic ecotoxicity and terrestrial ecotoxicity, acidification, photochemical oxidant formation, and eutrophication. Regenerated cellulosic fibers do not present significant effects on ozone layer depletion, photochemical oxidant formation, human toxicity, freshwater aquatic ecotoxicity and eutrophication when compared to cotton and petrochemical-based fibers. However, viscose fiber produced in Asia has a large contribution to global warming, abiotic depletion, and acidification. Although viscose fiber has higher sustainability as compared to petrochemical-based fibers, it shows higher environmental impacts and therefore is less sustainable than cotton fiber. SeaCell fiber is a third-generation regenerated cellulosic fiber produced using an innovative Lyocell technique, in which seaweed containing vitamins, minerals, and trace elements are added to the wood pulp before spinning. As a result, the produced fiber provides health-promoting and skincare effects. This fiber possesses softness and breathability, providing a pleasant feeling of well-being and is becoming very popular in sportswear and yoga attire as well as in sheets, towels, blankets, and baby clothing. This fiber has similar sustainability aspects to Lyocell fiber.

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Application of Biotechnology in the Processing of Textile Fabrics

Shanthi Radhakrishnan

Abstract Biotechnology, a new impetus in the last few years, has seen rapid developments in genetic manipulation techniques (genetic engineering) which introduces the possibility of producing organisms in order to optimize the production of established or novel metabolites of commercial importance and of transferring genetic material (genes) from one organism to another. Industrial biotechnology is the application of technical advances in life sciences to develop commercial products or to incorporate in industrial processes. Enzymes are being used in numerous new applications in the food, feed, agriculture, paper, leather, and textile industries which results in enhanced product quality along with significant reductions in cost and environmental pollution. The potential to harness biotechnology and produce new or modified fibers as well as improving the production yields of existing fibers is being studied. Novel fiber-forming biopolymers with biocompatibility and biodegradability are now being manufactured using large-scale fermentation equipment for medical applications. Natural biological fibers from natural raw materials possessing properties of synthetic fibers have entered the textile field. Enzymatic processes have replaced chemical methodologies in textile manufacturing to obtain a sustainable biobased economy. Biological processes play a major role in the removal of contaminants. The elimination of a wide range of waste materials and polluting substances from the environment is an absolute requirement to promote a sustainable development of our society with low environmental impact. Without such advances in science and technology, the move to a more biobased economy would result in rapid depletion of renewable resources and environmental degradation. The natural protein molecules, enzymes, have paved the way for interdisciplinary partnerships with various textile applications for exploring new avenues in the textile industry. Further research is required for the implementation of commercial enzyme-based processes for the biomodification of synthetic and natural fibers.

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1 Introduction to Industrial Biotechnology

1.1 Meaning and Importance

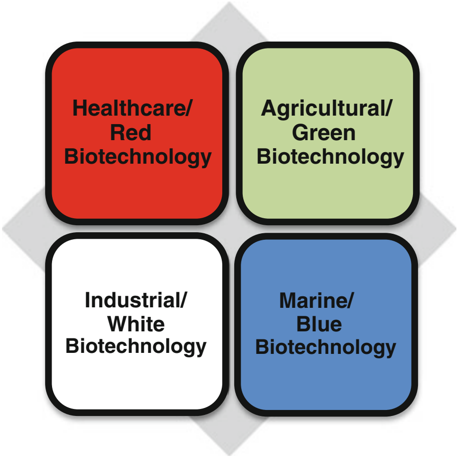
With the continued pace of world economic growth, sustainable socioeconomic development will depend upon a secure supply of raw material inputs for agriculture, industry, energy, and related sectors. Currently there is a heavy reliance on nonrenewable resources, namely fossil fuels and various minerals and chemical and thermochemical processes. The role of biological processes in the global economy is small but is growing fast as there are initiatives from both the public and private sectors that support the supply of industrial products and energy needs through biological processes and/or biomass resources. The biobased economy can be explained as consisting of those sectors that derive a majority of their market value from biological processes and/or products derived from natural materials, as opposed to products and processes associated with nonrenewable resources or purely chemical processes [1].

A sustainable raw material supply is one of the most important issues for the transition towards a biobased economy. Hence the resource base needs to be recognized from the perspective of supply and demand. The biomass that is to be exploited is obtained from many sources such as specially grown crops, waste materials of food and fodder production, and residues from forest and marine sources. Potential resources for biobased products and services also include municipal waste, manure, and animal products. Areas where biobased products and processes can substitute for mineral-based products, fossil, or chemical processes would serve to be of high importance in a bioeconomy. This substitution would help to make various industrial sectors become more sustainable in the long run and would also help in reducing greenhouse gas emissions and requirements for land disposal [2].

Biotechnology is the foundation for biobased products and services from a sustainable raw material supply to frame a bioeconomy. It helps to manufacture products intended to improve the quality of human life by using biological processes, organisms, or systems [3]. The Organization for Economic Co-operation and Development (OECD) has defined biotechnology as "the application of science and technology to living organisms, as well as parts, products and models thereof, to alter living or non-living materials for the production of knowledge, goods and services." In other words, biotechnology is derived from biological knowledge and finally is associated with the evolution of biological science. In short, biotechnology harnesses cellular and biomolecular processes to develop technologies and products that help improve our lives and the health of our planet [4].

The science of biotechnology can be divided into subdisciplines called red, white, green, and blue as given in Fig. 1.

Fig. 1 Subdisciplines of biotechnology



- **Healthcare/Red Biotechnology** plays a vital role in drug discovery and is improving outcomes for patients today and addressing the medical needs for the future.
- **Agricultural/Green Biotechnology** or plant biotechnology provides farmers with the technology to grow food, feed, fuel, and fiber with less input and less impact on the environment.
- **Industrial/White Biotechnology** uses fungi, yeasts, bacteria, and/or enzymes as cell factories to make sustainable energy, chemicals, detergents, vitamins, paper, and a host of other everyday things.
- **Marine/Blue Biotechnology** includes processes in marine and aquatic environments, such as controlling the multiplication of harmful waterborne organisms [3].

The role of biotechnology in different application areas is multifold. As healthcare has become a significant part of government expenditure, many organizations have undertaken research that has brought many medical innovations that enhance the quality of life. Plant biotechnologies produce new high-yielding nutritious crops with disease and drought resistance. Biotechnology also plays a vital role in saving aquatic life and marine environments. White biotechnology has huge prospects in creating natural biobased products with biodegradability features, modifying and developing new processes with enzymes, using biomass as feedstock for the generation of fuels and energy, and also envisaging drastic reductions in environmental pollution and emissions. The use of proteins which form the basis of biotechnology in all walks of life highlight its importance in being a significant tool in producing useful biobased products for the development of human life.

1.2 Salient Features of Industrial Biotechnology

Industrial biotechnology, known as white biotechnology, is the use and application of biotechnology for industrial solutions, including manufacturing, alternative energy (or bioenergy), and biomaterials. It involves the practice of using microorganisms or components of cells, namely enzymes, to generate useful products of industrial importance. It uses biotechnology for industrial processing and production of chemicals, materials, and fuels. Components of microorganisms such as enzymes can generate industrially useful products, substances, and chemical building blocks with specific capabilities that conventional petrochemical processes cannot provide. The conversion of renewable biomass to products that are used in the consumer, chemical, or energy industries, is the most important characteristic of industrial biotechnology. Systems biology and synthetic biology may open new fields of application in any of the biotechnology areas by producing a new database of knowledge. Progress in nanobiotechnology and bioprocessing is needed in the next few years to bring biobased products into the market. It should extend from in vitro synthesis via cells to whole production processes and should be a vibrant part of the overall bioengineering strategy.

Nanobiotechnology has become a main contributor to green chemistry, where sugars or vegetable oils which are renewable resources are transformed into a variety of chemical substances such as fine and bulk chemicals, pharmaceuticals, biocolorants, solvents, bioplastics, vitamins, food additives, biopesticides, and biofuels. Apart from these substances many intermediate products are produced at different stages in the different value chains which are very complex and require analysis and experimentation. Biorefineries, which manufacture biotechnological products, have a strong interdisciplinary approach in producing biobased products. The wide and diverse applications of industrial biotechnology indicate that it is much more than a sole industrial or economic sector but form the basis for a biobased economy [5].

The aim of industrial biotechnology is to create biobased products and processes for sustenance. Certain techniques are handled by biotechnologists to carry out such work. They are.

- **DNA/RNA**: Genomics, pharmacogenomics, gene probes, genetic engineering, DNA/RNA sequencing/synthesis/amplification, gene expression profiling, and use of antisense technology
- **Proteins and other molecules**: Sequencing/synthesis/engineering of proteins and peptides (including large molecule hormones); improved delivery methods for large molecule drugs; proteomics, protein isolation and purification, signaling, identification of cell receptors
- **Cell and tissue culture and engineering**: Cell/tissue culture, tissue engineering (including tissue scaffolds and biomedical engineering), cellular fusion, vaccine/immune stimulants, embryo manipulation

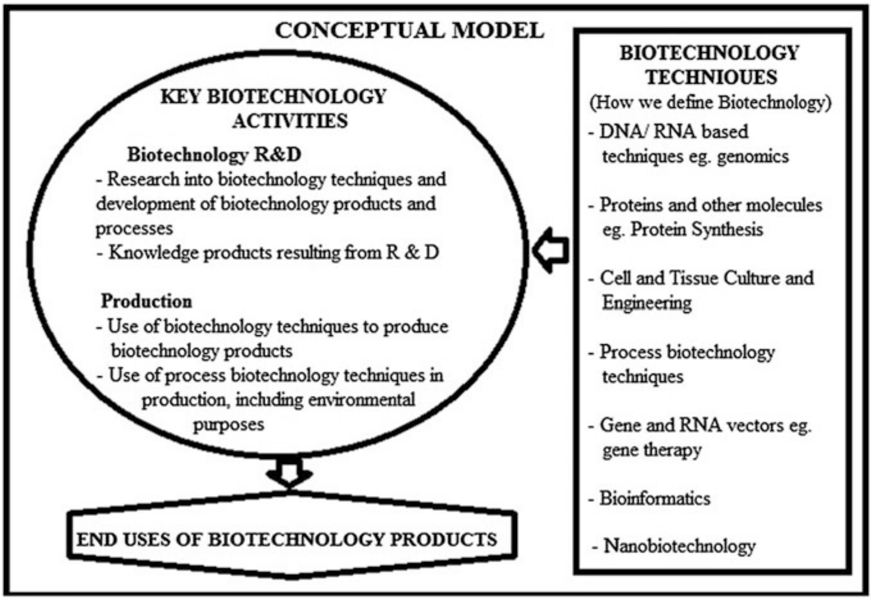


Fig. 2 Conceptual model of biotechnology [6]

- **Process biotechnology techniques**: Fermentation using bioreactors, bioprocessing, bioleaching, biopulping, biobleaching, biodesulphurization, bioremediation, biofiltration, and phytoremediation
- **Gene and RNA vectors**: Gene therapy, viral vectors
- **Bioinformatics**: Construction of databases on genomes, protein sequences; modeling complex biological processes, including systems biology
- **Nanobiotechnology**: Applies the tools and processes of nano/microfabrication to build devices for studying biosystems and applications in drug delivery, diagnostics, and the like [6]

Extensive research in the techniques used for biotechnology results in the development of biobased products and processes which creates a knowledge base for further research and development. These techniques are used in the production of biobased products and also in the processing sequence of industrial production resulting in environmental benefits. The conceptual model is given in Fig. 2.

The five core R&D areas of the USA Biomass program (Biomass Program USA, 2005) show the scope of industrial biotechnology and highlight the processes that use biomass to generate energy and finished products. The five core R&D areas of the Biomass program are shown in Fig. 3 [7].

Biorefineries that produce fuels, power, heat, chemicals, and other by-products use the huge supply of lignocellulosic biomass feedstock. The biomass is broken down into basic component sugars by means of chemical and biological processes

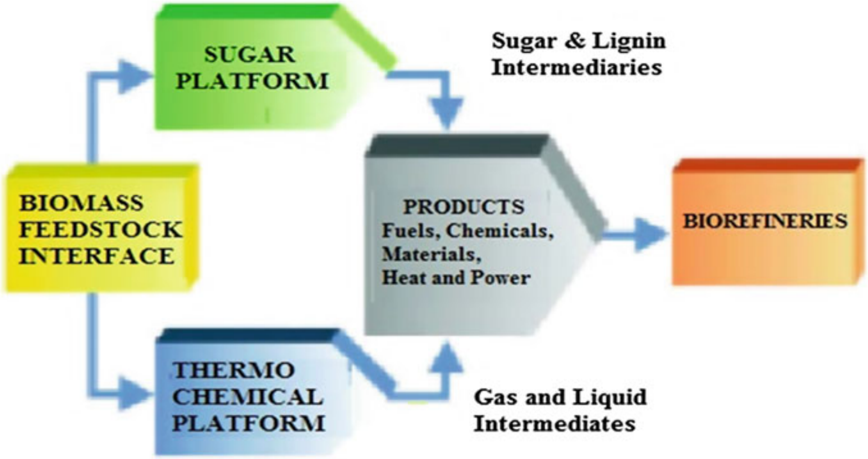


Fig. 3 Biomass program five core R&D areas [7]

as depicted in the sugar platform. The thermochemical platform performs the function of converting the biomass or biomass-derived residues to intermediates such as pyrolisis oil and syngas which can be used as raw fuels or products. These products can also be further refined to produce alternatives to existing commercial commodities such as oils, gasoline diesel, synthetic natural gas, and high-purity hydrogen. Maximum utilization of biomass takes place when integrated biorefineries convert the energy, sugar, and lignin intermediates into final products. The final products include a range of fuels, combined heat and power, chemicals, and materials that play a crucial role in sustainability [7].

1.3 Challenges Facing Industrial Biotechnology

Some of the challenges that face the growth of industrial biotechnology are green growth, climate change, and sustainable development.

1.3.1 Green Growth

Basically, any system that generates increasing prosperity coupled with the protection of natural systems that are sustainable, is termed a green economy. A major factor that can be a long-term driver for economic growth is the green concept, for example, investments made in efficient use of energy and raw materials and in renewable energy. This underlying principle of "going green" in industrial biotechnology can upgrade the performance of the industry and give value addition to the product. As this technology grows and matures, it will provide extensive viable green solutions for the healthy growth and sustenance of our environment.

1.3.2 Climate Change

Our planet has been severely misused ever since the industrial revolution took place under the name of economic growth. This principle has been challenged by industrial biotechnology and disrupts resource consumption by reviewing the conventional industrial processes. Alternatives and options for the traditional industrial processes can pave the way towards better economic growth along with savings in water, energy, raw materials, and reduction in waste. According to the World Wide Fund for Nature (WWF) report, the industrial biotechnology sector globally eludes the formation of 33 million tons of CO_2 each year through various applications of biotechnology, without taking ethanol use into consideration, while globally emitting 2 million tons of CO_2. This organization has also highlighted the potential of industrial biotechnology in building a green economy by reducing CO_2 emissions. The WWF report concludes that by 2030 the use of biotechnology processes and biobased products will reduce emissions between 1 billion and 2.5 billion tons CO_2 equivalent per year. This value represents more than Germany's total reported emissions in 1990 [1].

1.3.3 Sustainable Development

It is essential to estimate the impact of white biotechnology on sustainable development based on three elements, namely people, planet, and profit. The effect of industrial biotechnology on society is analyzed over a range of areas of societal concern namely employment (job retention/creation), innovation (development of new technology platforms), and responsibility (decrease in dependence of society on the usage of fossil resources). This would help to conserve resources for future generations.

The role of industrial biotechnology in decreasing the carbon footprint is very important as it is one of the greatest challenges facing the world. Due to increased process efficiency and renewable feedstock there is a reduction in greenhouse gas emissions, water and air pollution, raw material consumption, and waste production. The application of this technology in the most polluting chemical industry has paved the way for lower greenhouse gas emissions. This attribute helps to position industrial biotechnology as a great tool to address global warming.

Many industries such as chemicals, leather, textiles, animal feed, pulp and paper, energy, metals and minerals, and waste recycling are using biotechnology processes. When the uptake of biological industrial processes is fast, additional value is produced as lower costs in processing and raw materials. Furthermore, additional benefits are derived from smaller investments in fermentation plants and enhanced income from new or high-performance products [8].

The trend today is to question the sustainability aspect of all industrial, societal, and economic activity. Consumers want to know about the impact of their consumption and companies advertise their claims about the sustainability of their products. More than the lifecycle of products and services, the consumption of products by households accounts for more than 60 % of the impact. Industrial biotechnology has principles rooted in cleaner and greener concepts which leads to an economy that is not dependent on fossil fuels and industrial raw materials but on biorenewable carbon sources. The most promising strategy is the concept of biorefineries that work on the processing and fractionation of renewable raw materials to produce biobased products. Synthetic biology produces chemicals from natural pathways and from modified base materials which would open new areas of research and development. When industry becomes more sustainable there is scope for knowledge-driven professions, innovative technology platforms, and conservation of environment.

1.4 Role of Industrial Biotechnology for a Low Carbon Economy

Industrial biotechnology can enable a shift towards a biobased economy. A biobased economy is based on production systems that rely on biological processes and with natural ecosystems that use natural inputs, spend minimum amounts of energy, and do not produce waste as all materials discarded by one process are reused as inputs for another process. Biotech applications encourage new services, behavior, and institutional structures that result in reduced CO_2 emissions over the long term, giving rise to a low-carbon feedback. The contribution of industrial biotechnology may be summarized as improved efficiency, the substitution of fossil fuels and oil-based materials, and a closed loop system with the potential to eliminate waste. All four dimensions play an important role in reducing pollution and also play a vital role in the amount of carbon feedback they generate.

1.4.1 Improved Efficiency

Conventional industries, including the food, pulp and paper, leather, and textile industries, are using natural organisms or enzymes in a number of processes. This results in more efficient use of natural resources and lower energy usage during the production stage or in connected stages along the value chain. The resource usage, GHG emissions, and pollution are greatly reduced when biological methods are used in the lower rung of the value chains and the efficiency is multiplied at the end of the production chains. Industrial biotechnology is expected to penetrate the market with energy-saving efficient solutions and grow, giving great benefits and advantages in conserving the environment.

Efficiency gains and resources can be spent on low GHG investments and knowledge, infrastructure, and processes that can be adopted to reduce carbon feedback. In industries, biotech applications enable the use of smaller areas of land. This land can be used for other biobased applications that will bring many benefits.

1.4.2 Switching to Biofuels

The use of biofuels and their adoption in industrial processes has given rise to the substitution of fossil fuels by about 20 %. It has been reported that this substitution has the capacity to reduce one billion tons of emissions by 2030. Without the speedy introduction of second-generation biofuels, the emission reduction potential would be 50 % lower at 530 Mt CO_2e. Creation of infrastructure and essential logistical systems are some of the dynamic effects of the innovative biotechnologies in the biofuel production sector.

The basic chemical, ethanol, can be used for the production of a variety of other compounds. There is a low-carbon feedback when biotechnological processes is used for the production of biobased materials which is based on the ability to produce large volumes of bioethanol efficiently. The switchover from fossil fuels to biofuels will help the growth of short-term emissions and promote the development of technologies and infrastructures that will help to establish a very strong market for biobased materials. This process will further assist in bringing down GHG emissions and increase low-carbon feedback on a long-term basis [9].

1.4.3 Replacing Petrochemicals with Biobased Material

Many petrochemicals such as HDPE (high-density polyethylene), PTT (polytrimethylene terephthalate), Nylon 6, PET (polyethylene terephthalate), ethyl lactate, and maleic anhydride have been replaced by biobased chemicals. A number of biorefineries have developed which produce a wide range of chemicals and end-products. A huge amount of waste reduction results as the biorefineries can work on the remains of production which enter as raw material for the next production cycle. On analyzing the lifecycle of biobased products there have been significant reductions in energy consumption and GHG emissions showing that these processes have a low-carbon feedback.

1.4.4 Closing the Loop

The carbon present in waste streams forms a valuable source for energy generation. It has been estimated by the Intergovernmental Panel for Climate Change (IPCC) that approximately 900 Mt of such waste was produced worldwide in 2002, and over 33 tons of BOD^{16}/day were present in industrial wastewaters.

When carbon is disposed of in anaerobic conditions, methane may be produced, and if it is released into the atmosphere it can cause global warming. Biogas harvested from digesters and wastewater streams may be utilized for many applications reducing energy consumption from fossil fuels. The biotechnology solutions for waste management systems reduce the negative impact of existing systems by recycling the natural carbon as feedstock [9].

Hence biorefineries help to transform any biobased materials into feedstock which in turn produces biomaterials or biofuels. The gap between waste and production will be eliminated as many systems that are created produce less waste and the organic materials produced and disposed of after consumption, re-enter the production cycle of biorefineries as feedstock. Thus biorefineries can close the loop between waste and production and give advantages including the ability to produce biobased materials with fewer GHG emissions and the creation of bio-based renewable carbon stored in end-products to be reused continuously for forthcoming production processes.

2 Fibers and Biopolymers

Advancements in chemistry and materials science have given rise to a number of novel synthetic polymers such as nylon, polyethylene, and polyurethane over the past century. These polymers are produced from nonrenewable resources and are not biodegradable. Their strength and durability make them remain in some form in the environment and create problems in disposal. During the production of synthetic polymers toxic chemicals are used and toxic by-products are generated. Currently great attention has been focused on biopolymers that are derived from natural raw materials or may be produced using modern technologies having biotechnical origin.

The growth of industrialization over the past century has raised issues about patterns of production and consumption. As the economic activities around the globe have increased 50-fold, the impact of industrial practices on the environment have been the focus of many environmentalists. Great attention has been focused on the concept of sustainable economic systems that are based on renewable sources of energy and materials. Biopolymers, which are derived from biological origin, would emerge as an important factor in economic development. Biopolymers are used in many applications including packing industrial chemicals, medical implant devices, and computer storage media. The manufacturing systems used to create biopolymers would help in minimizing energy consumption and waste generation [10].

2.1 Green Polymers

Green polymers are biodegradable recyclable biopolymers from renewable resources. The raw materials for the production of these polymers may be either renewable (based on agricultural plant or animal products) or synthetic. There are four main types of green polymer, namely:

- ***Starch-Based Polymers***—Found as granules in plant tissue and can be modified to be melted and deformed thermoplastically (injection molding and extruding). They have good oxygen barrier properties but can sustain only brief contact with water.
- ***Sugar-Based Polymers***—Polyhydroxibutyrate is made from sucrose or starch by a process of bacterial fermentation; polylactides (lactic acid polymers) are made from lactic acid, made from lactose (or milk sugar). It can be formed by injection molding, blowing, and vacuum forming; and used for medical applications, for example, surgical implants that do not require removal by operation.
- ***Cellulose-Based Polymers***—The use of cellulose as raw material for making packaging material such as cellophane has been established. It material may be available in the form of pure cellulose or of a nitrocellulose coating that is biodegradable; applications of cellophane include packaging for confectionery and cigarettes.
- ***Synthetic Materials-Based Polymers***—The high price of biodegradable polymers from synthetic raw materials, for example, aliphatic aromatic copolyesters, makes them unsuitable for consumption. Large-scale production will increase availability and reduce prices. These polymers are used for making substrate mats.

Biopolymers are renewable because they are made from plant materials such as agricultural nonfood crops, which can be grown indefinitely. Hence, the use of biopolymers would create a sustainable industry when compared to the feedstock derived from petrochemicals that will diminish and die out eventually. In addition, biopolymers have the prospective to reduce carbon emissions and minimize CO_2 quantities in the atmosphere. During the degradation of biopolymers CO_2 is released and these gases are reabsorbed by crops grown for raw material, making this process carbon neutral. There is an interest for biopolymers among consumers as they believe that conventional plastics are not eco-friendly to the environment [11].

Textiles are made up of fibers that are giant molecules called polymers. Polymers are made up of several molecules called monomers that are able to bond to form long chains. This linking up of monomers is called polymerization Monomers form polymers by addition or condensation reactions; for example, nylon is a condensation polymer [12]. The structure of the monomer and polymer are given in Fig. 4.

Most polymers are obtained from petroleum products and crude oil but some polymers may be available in nature. Chemically they are based on carbon

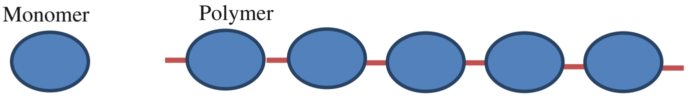


Fig. 4 Structure of the monomer and polymer

although some polymers are based on noncarbon compounds. Natural biopolymers contain macromolecules produced by living organisms such as starch or proteins whereas synthetic biopolymers have macromolecules manufactured from biomolecules. When biomass monomer forms the basis of polymers, they are termed "renewable polymers." This is because the source can be replaced by growing more biomass and repeating the process of extraction. Moreover, the source should also be replenished at a pace that equals or is faster than the rate of consumption. Biopolymers, which include polysaccharides, polyesters, and polyamides, are produced from natural processes with the help of microorganisms. The properties may be based on the composition and molecular weight of the polymer and may be available from viscous solutions to plastics. Genetic engineering plays a vital role in the manipulation of microorganisms which helps in producing biopolymers with predetermined properties suitable for special medical applications such as tissue engineering and drug delivery [13, 14].

To manufacture sustainable new textile fibers, two different approaches may be adopted. Genetic engineering forms the base of one method where suitably designed genes are tailor-made to make monomeric protein molecules. These molecules are separated and converted into fibers. In the second case transgenesis is followed where modification of fibers is undertaken and other proteins are expressed internally, for example, cotton with high strength characteristics and colored cotton [12].

2.2 New and Modified Raw Materials

2.2.1 Cellulose-Based Fiber

- Cotton (biopesticides, BT cotton, colored cotton)

The domination of natural fibers especially cotton continues with approximately 20 million tons grown/year by about 85 countries. This fiber is a highly essential tool for bringing about change in the technical and economic sectors. Some of the major problems facing cotton cultivators have been addressed by biotechnological means in two ways. The first method is to develop improved resistance to insects, diseases, and herbicides which is a short-term approach. Development of cotton fiber with modified properties such as improved strength, length, appearance, maturity, and color, seems to be the long-term directive [15, 16].

- Transgenic Cotton

One of the major cotton pests, the pink bollworm, has been destroyed by the use of a completely new kind of biotechnology tool. A toxin gene from a soil bacterium called BT is inserted into the cotton plants to create a caterpillar-resistant variety. Monsanto scientists report that the gene is DNA that carries the instructions for producing a toxic protein that kills caterpillars by paralyzing their guts when consumed. Plants with the Bt toxin gene produce their own toxin and thus can kill caterpillars throughout the season without being sprayed with insecticide. This variety is safe for the public and the environment as it attacks only the caterpillars and is harmless to other organisms. This Bt gene technology for transgenic cotton has been registered under the trademark Bollgard® and the cotton variety carrying the patented gene can be cultivated by obtaining seeds from authorized seed companies. Other Bts are now being developed for the suppression of loopers and other worms in cotton as the use of insecticides is challenging the green image of cotton. A "wound-inducible promoter" gene capable of producing a localized dose of toxin within 30–40 s of insect biting, is being developed for insect resistance [15].

- Colored Cotton

Oligo-genes which give color to cotton, are genes that contain chromosomes. Colored cotton is a naturally colored fiber with color in the lumen area. The application of color is by two methods, namely conventional genetic selection and by direct DNA engineering [17]. DNA engineering crosses the colored strain Gossypium hirsutum with a white strain to produce hybrids with better qualities such as fiber length, strength, and color fastness when compared to the parents of colored cotton [11, 15].

Naturally colored cotton in deep fast shades would help to change the face of the wet processing industry. Based on the colored intensity of lint, Gossypium species are grouped into different color groups, namely *aridum, hirsutum* (brown), *arboretum, harbaceum* (medium brown), *armourianum, mustlinum, anomalum* (very light brown)*, arboreum* (Khaki), and *hirsutum* (Green). Pollution and hazards due to dyeing will be greatly reduced by natural blue cotton and would serve to be an important savior in jeans production. The process is aimed at the jeans market ($10 billion in the United States and £800 million in the United Kingdom) and involves the transfer of a gene from a blue flower to the cotton plant [10]. Further research and development are aimed to modify the cotton plant genetically to yield colored cotton with modified properties in physical properties and pesticide and herbicide resistance. The color range is limited and there is a small niche market for colored cottons. The future dream of textile industries will be to sell their products under the eco-friendly banner by using transgenic intensely colored cottons (blues and vivid reds), which is nature's gift to preserve the environment [16, 18, 19].

- Hybrid Cotton

Polyhydroxybutyrate (PHB) is a natural polyester grown in the hollow core of the hybrid cotton fiber, thereby creating a natural polyester/cotton fiber. A 1 % polyester content has contributed to 8–9 % heat retention in the end-product. Other fibers and proteins may be introduced to suit various needs. New properties that enhance the performance of the end-products could be introduced such as greater fiber strength, enhanced dyeability, improved dimensional stability, reduced tendency for shrinking and wrinkling, and altered absorbency. To reduce pollution by pretreating fibers with fewer pectins, waxy materials, and containing enzymes that can biodegrade environmental contaminants could be engineered to assist in the filtration of contaminated water [15].

2.2.2 Protein-Based Fibers

- Spider Silk

Spider dragline silk is a marvelous material that has been engineered to be five times as strong as steel, twice as elastic as nylon, waterproof, stretchable, and exhibit the unusual behavior that the strain required to cause failure actually increases with increasing deformation. A goat embryo is genetically combined with spider DNA, when the goats with modified genes produce milk which contain spider silk. The fibers retrieved from goat milk are made of a polymerized protein fibroine and are reported to be stronger than Kevlar and could be used for making bulletproof vests [20]. Advantageous textile properties have been transferred to microorganisms that are multiplied by bulk fermentation processes. Similarly spider DNA is transferred into bacteria to manufacture proteins with increased strength and resilience of spider silk [16, 21].

- Naturally Colored Silk

Worldwide attempts have been made for producing natural colored silk by modifying the genes of silkworms. The Kyoto Institute of technology, Japan, has taken the credit for producing fluorescent green silk by genetic alteration of the silkworm. Carotenoids, carotenes, and xanthophylls derived from mulberry leaves have been used to color the cocoons and are found to be appearing in the sericin which coats the fibroin of the silk filament. However, based on the pigment permeability on the different parts of the cocoon, the genetic constitution of the silk glands, and the differences in fiber pigment according to the color of the cocoon, variations in color seem to occur. The gene modification technologies are very difficult and are under research and development [19].

- Wool

Biotechnology has various new tools that would influence animal fiber production. New technologies in animal breeding and health care include in vitro fertilization, embryo transfer, diagnostics, genetically engineered vaccines, and therapeutic drugs. Extensive research in genetic modification of sheep has been undertaken by Australia's national research organization, CSIRO. Resistance to the attack of blowfly larvae has been developed by modifying the sheep to secrete an insect repellent from the hair follicles to drive off the insect. Biotechnology-based "artificial epidermal growth factor" is injected into the sheep to interfere with hair growth. Breaks appear in the hair follicles of the sheep after a month and the fleece is pulled off, saving energy and time. Much research has been undertaken by countries all around the world to produce fine valuable wool through the use of biotechnology [15, 16, 18].

2.3 New Fiber Sources

2.3.1 Bacterial Cellulose

Bacterial cellulose is cellulose produced from bacterial origin and not from plant origin. The bacteria employed for cellulose production is Acetobacter xylinium because it produces good amounts of cellulose, making it industrially viable as the cellulose can be produced from a variety of substrates. Cellulose produced from bacterial origin is pure in nature and does not contain other compounds such as lignin or hemicellulose seen in plants. Similar to polymerization, the cellulose is formed as an extracellular polysaccharide with the appearance of a ribbon-like structure. Bacterial cellulose is characterized by properties including high tensile and tear resistance and good hydrophilicity that differentiates it from plant cellulose. Sony Corporation of Japan uses bacterial cellulose in acoustic diaphragms for audio speakers. Other applications include the production of activated carbon fiber sheets for absorption of toxic gas, as thickeners for special cosmetic applications, and as reinforcing material with aramid fibers. It is used as a skin substitute and in wound-healing bandages in the field of medicine [11, 19]. Furthermore, in vitro cultivation of plant cells would produce a secure supply of pure cellulose not bound by climatic or geographic limitations [18].

2.3.2 Biopolymers for Wound Dressing

Polysaccharides, chitins, alginate, dextran, and hyaluronic acid are some of the biopolymers used for wound healing in the field of medicine. Chitin, found in the shells of crustaceans, consists of long linear polymeric molecules of β-(1-4) linked glycans and with aminated, acetylated carbon atom. Fabrics produced with chitins are antimicrobial and antifungal in nature and are converted to end-products such as wound dressings and stockings. Chitosan is used in fabric finishing, wool shrink proofing, filtration systems, and recovery of materials including precious metals and dyestuffs from wastewater. Many industries are employing biomaterials for the development of new eco-friendly products. Courtaulds markets calcium alginate fiber-based wound dressing under the brand name “Sorbsan.” Many species of bacteria such as Leuconostoc mesenteroides are used for the fermentation of sucrose to produce Dextran, a fibrous nonwoven for special end uses including wound dressings. A British biotechnology company, Fermentech, is producing hyaluronic acid through fermentation. Hyaluronic acid, found in the connective tissue of vertebrates and in the capsules of some bacteria, is a polydisaccharide of *D*-glucuronic acid and *N*-acetyl glucosamine. This biopolymer is now available in large scale proving that biopolymer production has increased and manufacturers are following biotechnological processes for a clean and green production of industrial products [15, 18].

2.3.3 Biopolymers for Bioplastics

The application of biotechnology for industrial processes has opened the doors to sustainable development. Alternatives to nonbiodegradable plastics is the highest goal in industrial biotechnology. The term *bioplastics* means biodegradable plastics made from various sources such as plant material sources as modified polymers or polymers made by microorganisms or plants and by polymers made from monomers obtained by fermentation. It has been estimated that the production of biobased polymers on the global level was 0.36 billion tonnes in 2007 and its market share is expected to be 10–20 % by 2020 [1, 22]. Some of the biomaterials available across the world have been discussed herewith.

The project, “Living Chemistry for Quality of Life” has been taken up by an Italian research group Novamont where agriculture, the environment, and chemistry are integrated to serve mankind. Mater-Bi® is a biopolymer that uses maize starch as the raw material for production. This is the first biopolymer made from agricultural sources and the chemical structure developed during photosynthesis is also preserved. Starch and other biodegradable agents are combined to produce an array of molecular superstructures with a wide range of properties. The biodegradable agents may be from renewable or synthetic sources or a combination of the two. Mater-Bi can be converted easily to products that have properties even better than traditional plastics. These products are biodegradable and compostable in a single composting cycle [23, 24].

Polyhydroxyalkanoate-based bioplastic marketed as “Mirel” by Cambridge has been certified as soil and marine degradable there by making it sustainable and eco-friendly. The polylactic acid fiber is made from lactic acid which is obtained by the fermentation of corn starch. This fiber termed “Lactron” has strength, stretch, and many other properties equivalent to nylon and polyester. Lactron, manufactured by Kanebo Spinning and Kanebo Gohsen of Japan, is available as yarn, thread, and woven and nonwoven fabrics. Another biodegradable fiber from corn is “Ecodear” manufactured by Toray Industries. Spare-tire covers and floor mats are made of this new sustainable material for the Toyota Motor Company’s redesigned compact car Raum which was launched in 2003 [15, 25].

Biotechnology has utilized the carbon stored in plants by photosynthesis for the synthesis of a range of polylactide (PLA) (2-hydroxypropionic acid) biopolymers. These biopolymers under the brand name, “Ingeo” are patented by NatureWorks. A process of fermentation and separation is used to convert the carbon and other elements in these sugars into biopolymers. Injection molding, thermoforming, and extrusion are some of the methods used to convert the polylactide resin into products such as plastic goods, film applications, packaging, and textile uses. Properties including resistance to ultraviolet light, low flammability and smoke generation, and hydrophilicity make it a valuable fiber for blending with cotton and wool. Currently production is around 180,000 tons, but is expected to reach a target of over 800,000–950,000 tons by 2020. The demand for this sustainable fiber is currently outstripping growth in EU supply [20].

Another important eco-friendly fiber is DuPont^{TM} “Sorona” made from corn. The partnership of scientists from DuPont and Genencor resulted in the development of the organism that would utilize glucose from corn starch to produce PDO. A special fermentation process was followed by a cleaning and distillation step, to obtain a pure form of Bio-PDO^{TM}. Properties such as quick drying, permanent stain resistance, resiliency comparable to nylon, and softness equal to polyester make it suitable for automotive technical textiles including carpets, mats, and fabrics. Thus it offers fabrics with good performance characteristics and is compatible with different fibers for blending [19, 26, 27].

The synthetic biopolymer “Biopol,” produced currently, is formed by the fermentation of sugars by the bacterium Alcaligenes eutrophus. These bacteria grow in tanks with a carbon-based food source. The polymer produced is separated and purified. Attempts have been made to genetically engineer bacteria such as E. coli for the viable and economic production of PHA. Plants such as cress and potatoes have been genetically engineered to produce biopolymers instead of storing the starch. The resultant biopolymers have the same structure as those formed by bacteria [29].

A sustainable plastic “Green Polyethylene” is made from a renewable raw material, sugarcane, in contrast to traditional polyethylene which uses raw materials such as oil or natural gas. The sugarcane juice is fermented at the distillery to form ethanol. Ethanol is subjected to dehydration and is converted into green ethylene. This material undergoes polymerization when it is changed to Green Polyethylene. The Green Polyethylene process cycle is given in Fig. 5. Braskem’s Green Polyethylene is made from Brazilian sugarcane. During the production of Green Polyethylene, CO_2 from the atmosphere is captured and fixed thereby helping to reduce greenhouse gas emissions. It has been estimated that 1 kg of green PE captures 2.5 kg of carbon dioxide during sugarcane production as compared to the fossil-fuel-based PE which releases 2.5 kg of carbon dioxide per kg into the atmosphere [23, 28].

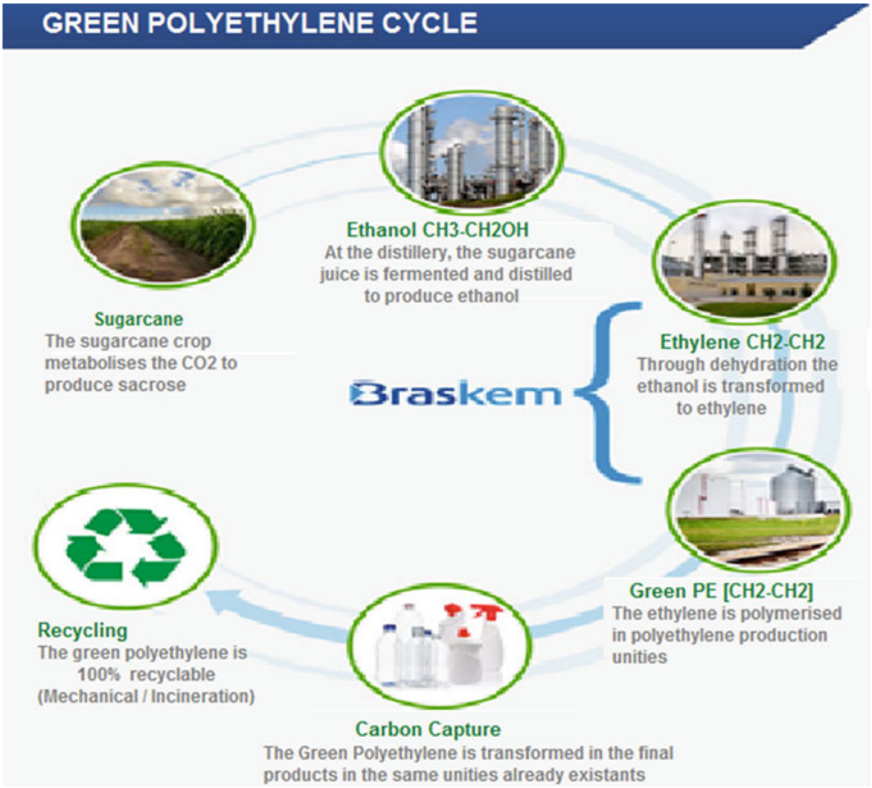


Fig. 5 Green polyethylene cycle [28]

2.4 Dyestuffs and Intermediates

Pigments that have been synthesized using the fermentation processes can serve as chromophores. On chemical modification they can produce dyes or pigments with a wide range of colors. Carotenoids, flavonoids, quinones, and rubramines are some of the stable pigments produced by microorganisms. It has been reported that fermentation processes have higher yield in pigments with lower residues when compared to animal and plant sources [30]. Both bacteria and fungi have been employed to synthesize dyes for the textile industry, for example, indigo. Some microfungi are capable of producing pigment up to 30 % of their biomass [21]. Certain fungal pigments have been from anthraquinone derivatives, which resemble vat dyes. Hence fungi can be used for the direct production of textile dyes or dye intermediates with the benefit of developing colored antimicrobial textiles. Colors developed from fungi include bright red pigment prodigiosin from *Vibrio spp*. and *Serratia marcescens*, bluish-purple from *Janthinobac-terium lividum*, violet pigment violacein from *Chromobac-terium violaceum*, and so on.

Currently the production of microbial pigments and evaluation as textile coloring agents is being analyzed at BTTG, Manchester, UK [31].

The use of soya bean for developing a wide range of products has been in existence for a long time. Recombinant genetic biotechnology has been used to alter the lipid profile of soya beans to provide a wider range of biohydrocarbons for industrial applications. The applications of amides, esters, and acetates of biohydrocarbons are varied and used in the manufacture of plasticizers, antislip agents, and mold-release agents for synthetic polymers. When amines, alcohols, phosphates, and sulfur groups are linked with biohydrocarbons they can be used as fabric softeners, surfactants, emulsifiers, corrosion inhibitors, antistatic agents, hair conditioners, ink carriers, biodegradable solvents, cosmetic bases, and perfumes. Similarly with aluminum and magnesium, the biohydrocarbons are used to produce greases and lubricating materials. When the raw material for intermediaries and auxiliaries are renewable, the processing sequence would be green and sustainable leading to a clean environment [32].

3 Enzymes for Bioprocessing

Enzymes are biocatalysts made up of protein molecules that have specific functions depending on their complex structure. Enzymatic reaction takes place in a specific part of the enzyme called the active site the remaining parts of which act as a support framework. The amino acids of the protein molecules in the active site get attached to the substrate while the reaction takes place. Thus the enzyme is target specific as the other molecules in the enzyme will not fit into the active site due to incorrect shape.

In a reaction catalyzed by enzymes, the substrate gets attached to the active site to create an enzyme–substrate (ES) complex. The product formed is released thereby leaving the enzyme free for the next substrate molecule. The conditions inside the active site including pH, water concentration, and charge, are made congenial for the reaction to take place. These conditions are quite different from the environment outside the active site.

During enzyme reaction the substrate with higher energy will be converted into the product with lower energy levels to bring about equilibrium. It is always essential for the substrate to overcome the activation energy before it changes into the product. When the activation energy is large, the rate of reaction will be slow. However, the biological reactions that have large activation energies are quickened with the help of enzymes. In a reaction enzymes reduce the activation energy so that the kinetic energy of the molecules proceeds with the reaction.

There are many factors that affect the rate of enzyme reactions such as temperature, pH, enzyme concentration, substrate concentration, and inhibitors. Enzymes work best at optimum temperature. Because the enzyme and substrate molecules have more kinetic energy they collide more often, and a large number of molecules have sufficient energy to overcome the activation energy. pH is an important factor that affects the activity of the enzyme. Inappropriate pH affects the charge of the amino acids at the active site, so the properties of the active site change and the substrate can no longer bind. The enzyme concentration and substrate concentration are very important for the activity of the reaction. As the enzyme concentration and substrate concentration increase the rate of the reaction also increases, because there are more enzyme molecules creating more active sites available to catalyze the reaction. Therefore more enzyme–substrate complexes form. At higher concentrations adding more substrate does not make much difference, as the enzyme molecules become saturated with substrate, and there are few free active sites.

Inhibitors inhibit the activity of enzymes, reducing the rate of their reactions. They may be competitor, noncompetitor, or feedback type. A competitive inhibitor molecule has a similar structure to the substrate molecule and hence it can fit into the active site of the enzyme thereby competing with the substrate and slowing down the reaction. A noncompetitive inhibitor molecule is different in structure from the substrate and does not fit into the active site. It binds to another part of the enzyme molecule, changing the shape of the whole enzyme, including the active site, so that it can no longer bind substrate molecules. The feedback inhibitor works by regulating the reaction pathway. The activity of some enzymes is controlled by certain molecules binding to a specific regulatory (or allosteric) site on the enzyme, distinct from the active site. Different molecules can either inhibit or activate the enzyme, allowing control of the reaction rate. They are generally activated by the substrate of the pathway and inhibited by the product of the pathway, so the pathway is used only when it is needed. This process is known as feedback inhibition [33].

3.1 Amylases

After the fabric is woven the size material should be removed for further processing of the textile. The process of removing the size material from the woven fabric is known as desizing. During enzymatic desizing, certain starch degrading enzymes such as amylases are used to reduce the molecular weight of amylose and amylopectin molecules of the starch. This makes the starch water soluble and it is removed by a washing process. According to the type of sugars produced the starch hydrolyzing enzymes are classified as α-amylases, β-amylases, and iso-amylases. The most commonly used amylase for industrial processes are from filamentous fungal and bacterial sources [34].

Starch is made up of a mixture of two polymers namely amylose, a linear polymer, and amylopectin, a branched polymer. In amylose, several thousand glucose molecules form the linear polymer which is made up of glucose residues joined by an α-1,4 glycosidic bond. In amylopectin, the branched polymer has glucose residues joined by either the α-1,4 or α-1,6 glycosidic bond. The source of starch will determine the proportion of the two polymers. A combination of α-amylases, β-amylases, and iso-amylases will help in the complete removal of the starch molecules. These amylases are further classified as endo-acting and exo-acting enzymes. α-amylases are endo-acting and hydrolyze linkages randomly in both amylose and amylopectin, creating linear and branched oligosaccharides. Starch is degraded to shorter polymeric fragments called dextrins and maltose which are disaccharide and contain two glucose residues. In the case of β-amylase and iso-amylase they are exo-acting enzymes and attack the substrate from the nonreducing end, producing oligo- or monosaccharides [35].

3.2 Pectinases

A group of enzymes called pectinases are used for the degradation of pectic substances. Pectic substances are polysaccharides present in plant cell walls in the middle lamella region. Pectin-degrading enzymes are referred to as pectic enzymes and include pectolyase, pectozyme, and polygalacturonase. Pectin is a jellylike substance that unites the plant cells. Cellulose fibrils are embedded in this substance. Polygalacturonase is the commonly used enzyme that involves the degradation of plant materials.

An efficient enzyme which belongs to the family of pectinases is the enzyme pectate lyase. It facilitates the hydrolysis of pectins which are the salts of polygalacturonic acids in the primary wall matrix. In the biopreparation bath, the enzymes hydrolyze the biological cement, pectin, and the noncellulosic components of the primary wall are released and emulsified by the surfactants and mild chelating agents. The enzymatic hydrolysis of pectin in cotton fiber primary wall with alkaline pectate lyase is shown in Fig. 6. This enzyme works in alkaline conditions therefore it is beneficial for pretreatment processes. The loss percentage in weight and strength is lower when compared to conventional scouring. Only a small amount of wax present in the fiber is reduced, creating a good feel and hand [36].

3.3 Catalase

Bleaching is a process of removing the natural color and imparting whiteness to the material. The commonly used bleach is hydrogen peroxide. The efficiency and evenness of dyeing is dependent on the complete removal of the bleach before dyeing. Extensive use of water and energy is avoided by the use of catalase enzyme. The enzyme breaks the hydrogen peroxide to nonreactive molecules of oxygen and water under mild temperature conditions.

$$2H_2O_2 \xrightarrow{\text{Catalase}} O_2 + 2H_2O$$

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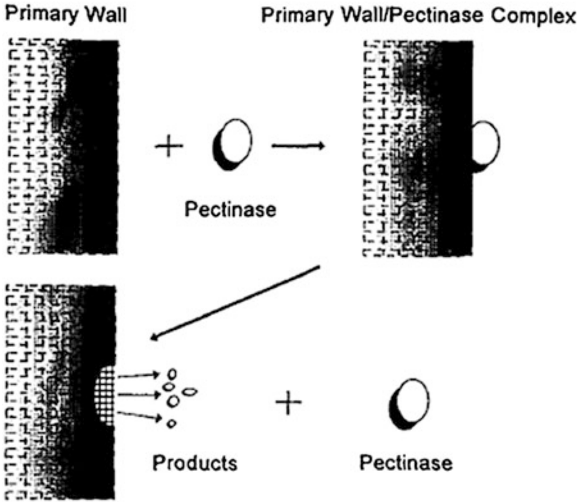


Fig. 6 Schematic of enzymatic hydrolysis of pectin in cotton fiber primary wall with alkaline pectate lyase [36]

The activity of the enzyme is 10 KCIU/g. One KCIU activity unit (kilo catalase international unit) is the amount of enzyme that breaks down 1mM of hydrogen peroxide per minute under standard conditions, namely 50 °C, pH 7.0, 10 mM H_2O_2 [37].

3.4 Proteases

Wool is a protein fiber that is hydrophobic in nature. This is due to the fatty acids in the epicutical surface membranes and the impurities such as wax and grease. Alkaline scouring using sodium carbonate, pretreatment using potassium permanganate, sodium sulphite, or hydrogen peroxide treatment is undertaken to remove these substances. Another disadvantage of wool fiber is the tendency to felt and shrink on wet processing. The small particle size of the protease enzyme facilitates entry into the fiber cortex causing damage to the fiber. Microbial transglutaminases (MTG) are a group of thiol enzymes that prevents damage caused by the protease enzyme. They catalyze the posttranslational modification of proteins by protein-to-protein cross-linking through the covalent conjugation of polyamines, lipid esterification, or by the deamidation of glutamine residues. MTG can catalyze acyl transfer by forming covalent crosslinks among proteins, peptides, and primary amines. This leads to an increase in protein stability and resistance to chemical and protease degradation. Moreover, they do not require calcium for activity and have a broad substrate specificity with low production cost. These properties are advantageous for industrial applications.

Transglutaminase-treated wool shows shrink resistance, tensile strength retention, handle, softness, wettability, and consequently dye uptake, as well as reduction of felting tendency and protection from the use of common detergents. Research and development in the application of these enzymes on leather and wool is underway [38, 39].

Cysteine proteases help in the hydrolysis of many compounds and can be divided into exopeptidases (e.g., cathepsin X, carboxypeptidase B) and endopeptidases (papain, bromelain, ficain, cathepsins). The peptide bond proximal to the amino or carboxy termini of the substrate is cleaved by exopeptidases whereas endopeptidases cleave peptide bonds distant from the N- or C-termini. Papain is the best-known cysteine protease that can cleave various peptide bonds and, therefore, have fairly broad specificity. Papain is used for the cocoon boiling and degumming of silk to remove the sericin, a proteinaceous substance that covers the fiber. Papain is also used to shrinkproof wool fabric [39].

3.5 Cellulase

The cellulose enzyme is produced by fungi embedded in soil and bacteria. This multicomponent enzyme is classified into three types depending on the activity range as acid cellulases, neutral cellulases, and alkaline cellulases. Acid cellulases work efficiently in pH lower than 7, whereas alkaline cellulases are active in a pH above 7. Endoglucalases (EGs) and cellobiohydrolase (CBHS) cellobiases are the active components in cellulases. The activity of the enzymes consist of three major steps, namely:

(1) Endoglucanases or β-1,4-glucanohydrolase: The endoglucanases attack the amorphous regions of the cellulose chains and randomly hydrolyze the cellulose polymers present along the chains which affects the interior of the polymer to generate new ends.
(2) Exoglucanases or β-1,4 glucan cellobiohydrolase: Here cellobiose is released by the action of exoglucanases on the nonreducing ends of the polymer chains.
(3) β-Glucosidase: The cellobiose formed in the previous stage is hydrolyzed into glucose by the action of β-glucosidase.

Cx
|
G—G—G—G - - G - - - - - - - - - G—G—G—G—G ---------- (1)

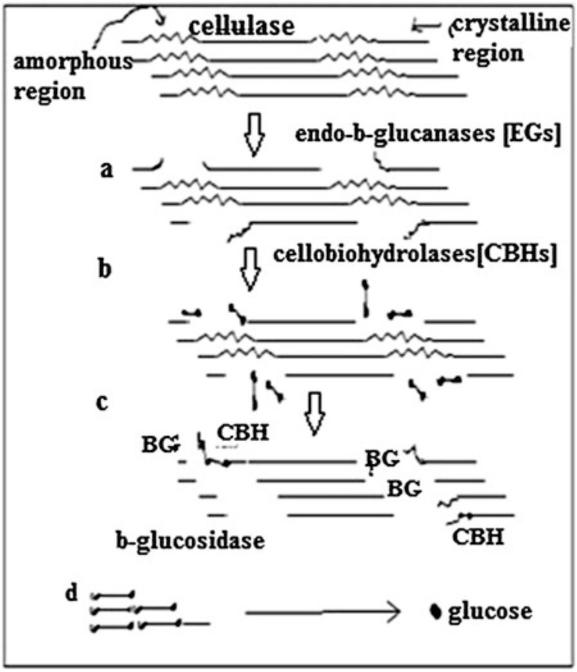
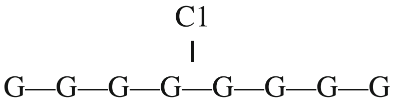
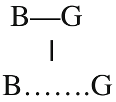


Fig. 7 Synergistic action of cellulase enzyme [40]



$$\text{G—G—G—}\overset{\text{C1}}{\overset{|}{\text{G}}}\text{—G—G—G—G}$$

------------ (2)



$$\begin{array}{c} \text{B—G} \\ | \\ \text{B.......G} \end{array}$$

------------ (3)

The three components of cellulase, endoglucanases, exoglucanases, and β-glucosidase work in harmony to convert cellulose to glucose. This is represented diagrammatically in Fig. 7. The β-glucose residues in the cellulose molecules are connected by the oxygen link called the 1,4-glucoside linkage. This link is formed by glucose condensation due to the elimination of water molecules in the cellulosic fiber. The cellulase enzyme acts on the 1,4-linkage of the glucose residues located in the cellulose molecules through catalytic reaction. By hydrolysis of this linkage, the long cellulose chains are converted to smaller chains which are further reduced to glucose [40, 41].

3.6 Laccases

Laccases (EC 1.10.3.2) are blue oxidase enzymes containing copper commonly found in plants, fungi, and microorganisms. This enzyme is dependent on oxygen as a second substrate for the enzymatic action. To detect laccases spectrophotometry is used with substrates such as ABTS, syringaldazine, 2,6-dimethoxyphenol, and dimethyl-p-phenylenediamine. The enzyme activity can be observed with the help of an oxygen sensor inasmuch as the oxidation of the substrate will occur by the reduction of oxygen to water. There are four copper centers that create monoelectronic oxidations of the substrate catalyzed by Type 1 copper. The transference of electrons from Type 1 copper to the trinuclear cluster of Type 2 and Type 3 copper brings about the reduction of oxygen and the release of water without the generation of toxic intermediaries. Nonenzymatic reactions such as ring cleavage of aromatics, crosslinking of monomers, and degradation of polymers can work on the oxidation products [42].

Laccase enzyme can decolorize many compounds making it a versatile biocatalyst for many applications especially in the field of dyeing and wastewater decolorization. It reacts with the insoluble indigo dye through a mediator compound, when electrons from the indigo dye are transferred to oxygen causing the cleavage of the double bond between the carbonyl groups of the indigo dye. Decolorization occurs due to the destruction of the dye chromatophore. Generally, textile dye effluents contain all types of dyes and auxiliaries in different combinations and successful decolorization of the effluent is a difficult task. A biodecolorization system that can maintain its activity upon contact with various dyes is essential. The oxidation of both phenolic and nonphenolic compounds can be performed with the help of laccase enzymes leading to the mineralization of a wide range of synthetic dyes. Thus laccase enzymes serve as a useful biological tool for several textile applications that would otherwise be very polluting in nature [43].

4 Innovative Biotextiles

Technical textiles have become an emerging area and these developments are due to the technological improvements and research that has been undertaken in this sector. Technical textiles represent 40 % of the entire textile production and the innovation aspect makes them the futuristic trends in the fast-growing textile industry. This field calls for the interdisciplinary conglomeration of diverse scientific fields that contribute to engineer several functions into one fabric which has endless applications in all walks of life. Technical textiles have become a vital part of industries including car manufacture, space technology, agriculture, and biomedical technology [44–46].

The role of biotechnology in producing these innovative textiles is extensive. The range of products may be wound dressings, marquee fabrics, or clothing for special technical applications. In all cases, biotechnology plays a major part in product development and intermediate processes. Taking nature as inspiration many micro and nano products have been developed with the integration of several disciplines such as nutrition sciences, environmental technology, and the textile industry. Many innovative projects have been developed by the collaboration of biotechnology with the textile industry [47, 48].

4.1 Medical Textiles

The medical field has many innovative materials and applications that may range from simple wound dressings to complex tissue engineering techniques and implants. Many biologists and engineers combine their ideas and develop highly technical biomaterials and implants and methods of making them compatible with the human body. A good example of this feature are the three-dimensional fleeces which promote the growth of cartilage cells of the patient. Textile implants refined with a touch of biotechnology will help to inhibit the wear and tear of bones and cartilage or help in the growth of the bones suitable for dental implants. Hence textiles provide the medium and biotechnology provides the technology for the development of medical textiles [44–46].

Many medical implants including vascular prosthesis, heart valves, and sutures use polymer materials proving to be great achievements in the surgical field. The most important issue in tissue regeneration is the controlled revascularization of epidermal tissue which requires naturally occurring porous polymeric supports on which the cells are seeded with the required factors for growth. In vitro growth of biological tissue can be performed by the use of textile materials as scaffolds. Thus tissue engineering forms an integral part of biotechnology [21]. Products such as composite mesh with absorbable and nonabsorbable barriers for intraperitoneal placement, macroporous mesh, and xenogeneic and allogenic biological meshes are some of the unique implants developed for tissue engineering [49].

In general and clinical practice there are many patients with vascular diseases encouraging surgeons to work closely with medical technologies and textile industries to develop artificial biomedical products for patients. Considerable diagnostic and therapeutic advances have given rise to the technology of prostheses that uses artificial biomedical tools such as biotextiles, or synthetic materials or parts used to replace body parts. This makes the natural replacement of defective body parts or transplantation obsolete. While performing grafting, the major problems associated with conventional ePTFE is suture hole bleeding and sweating which has been addressed by the use of a biomedical sealant. Sulzer Vascutek's hydrolyzable gelatin (water soluble protein) sealant called SEAL-PTFE$^{\text{TM}}$, is used to coat and seal the external surface of the graft preventing suture hole bleeding and sweating and excellent handling properties may be achieved with antibiotic bonding [50].

4.2 Healthcare Textiles

The role of fabrics with antibacterial and antiviral mechanisms are currently important to arrest infection and diseases. These mechanisms are considered essential in hygiene products used by many consumers. Many products such as antiviral towel rolls and antibacterial products are used in hospitals and hotels [44]. It has been reported that enzymatic pretreatment combined with the simultaneous deposition of biopolymers and nanoparticles under ultrasonic irradiation, have helped in eliminating infectious organisms from textiles used for medical applications. Furthermore these fabrics have improved adhesion of the antimicrobial nanoparticles and durability of the finish has been tested for 70 laundry cycles. These fabrics serve to fight nosocomial infections and hospital-acquired infections which are a major challenge facing hospitals. This research work has been carried out by scientists at the Universitat Politècnica de Catalunya Barcelona Tech (UPC) in Spain [51]. Another report states that antibacterial textiles for hospitals have been developed with the help of zinc and chitosan nanoparticles, enzymes, and ultrasound. This research serves to develop medical antibacterial textiles that prevent infections due to hospital gowns and sheets of hospital beds [52].

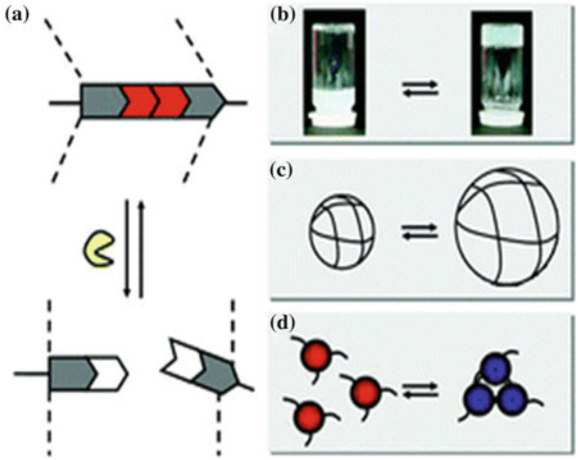
4.3 Intelligent Textiles

This segment of innovative textiles is multidisciplinary and requires expert knowledge from many fields. Intelligent textiles are those incorporating microsystems that help to measure and observe vital parameters such as blood pressure, pulse, or breathing [45, 46]. Other applications include sports and leisure wear that require thermoregulation based on incorporation of phase-change materials. The use of shape-memory materials for medical textiles and protective clothing is bringing about special functionalities to textiles. In an environment of extensive heat, these systems protect the body from getting overheated. In very high temperatures the shape-memory materials in the apparel produce an insulating layer by returning to their original shape. These textiles are used for uniforms of motor racing and gasoline pump attendants, and fire brigades, among others. Enzyme-catalyzed functionalization of fibers and immobilization of enzymes are two techniques that help in producing specialty fibers with unique functional characteristics [53].

4.3.1 Enzyme Responsive Materials

A class of materials that respond to stimulus and have a wide range of applications in biological settings is known as enzyme responsive materials (ERMs) [54]. These smart materials are highly sophisticated and undergo macroscopic

Fig. 8 Enzyme responsive action [55]



transitions by the activation of selective catalytic actions of enzymes. Extensive and new applications in the field of biology and medicine are possible through the use of enzymes as stimuli to generate a series of mechanical responses as shown in Fig. 8. The prospective applications are in the areas of regenerative medicine, diagnostics, and drug delivery. Based on technologies of supramolecular assemblies, chemically crosslinked gels, and (nanoparticle) surfaces, ERMs are divided into three different classes [55].

Over the past decade tremendous growth has been evident in the fundamental research of responsive polymers that are widely used in fields ranging from drug or gene nanocarriers, imaging, diagnostics, smart actuators, and adaptive coatings, to self-healing materials. A lot of research and experimentation has been undertaken in developing EMRs as per the end use. All living organisms and soft matter are susceptible to respond and adapt to external stimuli. This fundamental principle has formed the base of generating responsive polymers that undergo changes in chemical structures or physical properties that may be reversible or irreversible. These changes occur in response to specific signal inputs such as pH, temperature, ionic strength, light irradiation, mechanical force, electric and magnetic fields, and analyte of interest (e.g., ions, bioactive molecules) or a combination of them. The most favorable tool for triggering responses and reactions are enzymes and they have been used to design many special responsive polymers. Enzymes are an integrated part of all biological and metabolic processes of living organisms. The reactions catalyzed by enzymes are very selective, substrate specific, and work efficiently under mild conditions. The combination of enzyme-catalyzed reactions with responsive polymers opens a new opportunity for design flexibility and wide applications by equipping the responsive polymers with specific and selective triggering ability. The applications in the areas of drug controlled release, biocatalysis, imaging, sensing, and diagnostics is possible by using three different types of systems, namely enzyme-triggered self-assembly and aggregation of synthetic polymers, enzyme-driven disintegration and structural reorganization of polymeric assemblies and nanoparticles, and enzyme-triggered sol-to-gel and gel-to-sol transitions.

Enzyme-responsive biomaterials are very useful in the fields of regenerative medicine, diagnostics, and drug delivery. Because they respond to a biological signal they could be used in medical devices that release drugs on receiving a biological signal from a living cell. These materials function by detecting, responding, and ultimately mending biological processes. The first steps in engineering bioresponsive materials is to exercise control of the flow of molecules into and out of polymer particles by using specific enzyme controls and to mimic the in vivo feedback systems that control enzyme activity to enhance the response of these materials [56].

When transition of biopolymers occurs from one state to another based on the environment and requirement, they are termed as pH-sensitive and thermosensitive smart polymers. At the University of Washington, United States, researchers have developed a clever way to use smart polymers that provide size-selective switches to turn proteins on or off. If the smart polymer chain is attached to the protein molecule farther from the active site, the extended polymer chain would shield the side and prevent attachment of the macromolecule. However, when the polymer chain is coiled there will be no blockade for the macromolecule to bind with the active site. Such polymers could act as a kind of shield or molecular gatekeepers that regulate based on the size and kind of molecules that bind with the active site. Bioengineers could use this technology to control the functions of the proteins and design powerful diagnostic and sensing devices for medical applications [57, 58].

4.3.2 Biosensors

A device that identifies and quantifies chemical constituents of a substance (water, food, blood, or urine) from a sample is known as a biosensor [59]. They are diagnostic devices that integrate a biological or biologically derived material within a physicochemical transducer or transducing microsystem [32]. A bioassay or a bioanalytical system is different from biosensors in terms of requirement of additional processing steps such as reagent addition and construction of the device by permanent fixation of assay design [60]. The need for monitoring processes and a consciousness for better environmental control has motivated the development of biosensors to provide fast, reliable, and sensitive measurements with lower cost at on-site analysis.

Luminescent bacteria, *Vibrio fischeri*, are used to measure toxicity or biological impact from environmental samples such as water or soil. Measurement of cellular metabolism and assessment of toxic chemicals in aquatic samples is made possible by bacterial bioluminescence. Currently bioassay methods are integrated in biosensors, for example, Cellsense®. These are amperometric sensors that detect ions in a solution based on the electric current or changes in electric current. This sensor incorporates *Escherichia coli* bacterial cells for rapid ecotoxicity analysis. The electrons from the respiratory system of the immobilized bacteria of a suitable carbon electrode are diverted by applying a soluble electron mediator such as ferricyanine. The resultant current is a measure of bacterial respiratory activity, and change in the magnitude of the current indicates the agitation by pollutants [61].

The application of microbial capability to transform complex organic molecules into simpler inorganic constituents is known as bioremediation. There are many parameters that influence the growth of bacteria such as nutrient availability, metal ions, pH, dissolved oxygen, and temperature. Biosensors use the luciferase expression system to monitor these parameters for better control of the bioremediation process. The biological component in this molecular biosensor is a recombinant plasmid in which a foreign DNA fragment has been inserted. This also has an aspecific promoter, whose expression is sensitive to a target molecule. Biosensor-based methods can be used for the quick measurement and quantification of many substances, for example, BOD measurement. The biosensor consists of a microbial film centered between a porous cellulose membrane and a gas-permeable membrane as the biological recognition element. This film can bio-oxidize the organic substrate to be measured. A change in the concentration of dissolved oxygen or any other phenomenon such as light emission is taken as a response [62]. An amperometric sensor for measuring dissolved oxygen is used for measuring the bacterial respiration rate in close proximity to a transducer [61].

4.3.3 Novel Biocatalysts for Specific Applications

The development of biocatalysts to face special environments and the tailoring of efficient biocatalytic processes are the need of the hour for sustainability in industrial manufacturing. The biocatalytic processes in manufacturing include textile pretreatments, synthetic fiber modification (hybridization), and functionalization and biocatalysts such as extremozymes are able to withstand high temperatures, pH, and oxidative conditions in areas including fiber spinning and conventional textile wet processing. Some of the novel biocatalysts include those with specific on–off control for future processes and products based on functionalization of surfaces of textile membranes. Surface coating used as a tool for biofunctionalization of the existing range of synthetic and natural fiber substrates reduces the maturity time of new, customized functionalities such as moisture management and thermoregulation, breathability, self-cleaning, stain removal, wellness, and healthcare. This is based on regenerated protein, a combination of silk–wool protein-based systems and graft copolymerization of functional monomers onto fibers that have been initiated with enzymes [53].

4.3.4 Functional Finishes with Enzymes

An alternative to conventional finishing methods is functional coating methods that have many advantages such as not being affected by fabric type, use of low quantities of additives, and flexibility to make combinations of different

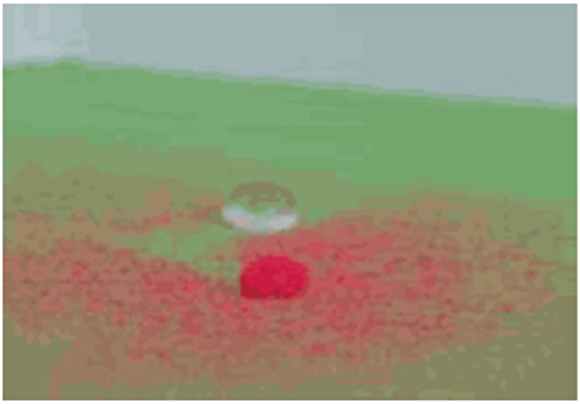


Fig. 9 Lotus effect finishes (*Source* BIOPRO)

functionalities in a simple manner. Some of the technologies include immobilization of enzymes, layer-by-layer assemblies, and nanocoatings. The permanent attachment of the enzyme to the textile substrate, so that it continues to catalyze the intended reactions again and again is known as enzyme immobilization. Wang et al. reported that the immobilization of lysozyme enzyme on wool with covalent bonds showed good antimicrobial effect against *S. aureus*. Immobilized preteolytic enzymes trypsin, lysosome, and lysoamidase on cotton, wool, and other dressings were found to be effective in healing wounds. The methods used for immobilization of the enzyme are adsorption, covalent bonding, entrapment, encapsulation, crosslinking, and nanocoatings. This concept reduces enzyme cost and provides a permanent bioactive textile substrate. The next technique is layer-by-layer assembly. In order to build a series of polyelectrolyte multilayer films on the substrate oppositely charged polycations and polyanions are sequentially adsorbed to form a layer-by-layer assembly. Functional molecules such as charged nanoparticles, dyes, and enzymes can be incorporated into the layers in a controlled manner to produce functional finishes on fabrics by using such assemblies [63]. Nano coatings get their inspiration from nature. Nature has come up with surfaces to which dirt is unable to attach due to complex micro and nanostructures. The self-cleaning effect of hydrophobic micro- and nanostructured plant surfaces was discovered and clarified by W. Barthlott at the University of Heidelberg in 1975. This is known as the “lotus effect” and is incorporated into textiles for outdoor clothing and marquees in retail stores. The lotus effect finish is presented in Fig. 9. Apart from these applications it is also useful in the medical field [64].

4.4 Packaging Textiles

Polylactide (PLA) is an innovative material from plant sources. It is commonly used in biodegradable catering dishes and packaging. Polylactide is a popular material used by apparel manufacturers for high-performance clothing and technical textiles.

PLA are fibers made from plant carbons when compared to nylon and polyester fibers which are made from nonrenewable petrol. PLA uses carbon that is absorbed by maize plants during photosynthesis from the air [45, 46].

5 Biotechnology for Sustainable Textiles

An ideal tool that reduces energy and material consumption and minimizes the generation of waste and emissions is modern biotechnology. Industrial biotechnology uses microorganisms and biological catalysts (enzymes) to produce clean industrial products and processes that will bring great benefits to industry over the next decade. Regulations are expected to intensify for both textiles and leather manufacture and the industries have to focus their attention on using less polluting technologies that generate less waste. Use of enzymes for a wide range of textile applications has been enhanced only in the past decade. Biotreatment in fiber preparation, pretreatment, and value-added finishing processes greatly affect effluent quality and cause reductions in effluent load. Savings will also be achieved in energy and water as enzymes are target specific and will work in mild conditions [32, 47].

The central feature of living systems is the facilitation of chemical reactions by catalytic proteins (enzymes). With protein engineering, enzyme-improved characteristics of specificity, selectivity, stability, and performance are being produced. The use of microbial enzymes in many other areas of the textile industry replacing existing chemical or mechanical processes is inevitable. Enzymes have been used in starch size removal by amylases, removal of hydrogen peroxide prior to dyeing by catalase, removal of fuzz from the surface of cellulosic fibers, and stonewashed effects by cellulases. The requirement for optical activity of chemicals such as polymer precursors is likely to grow.

The biocatalytic transformation of one chemical to another is defined as biotransformation. Certain cells, an extract from such cells, or an isolated enzyme may be used as the catalyst system of a specific reaction. The concentration of individual enzymes in cells is less than 1 %; gene amplification techniques can increase this percentage. Biotransformations will slowly overcome the production of bulk chemicals by oil-based processes and will transform the industrial processes into greener ones. The requirement for optical activity of chemicals such as polymer precursors is likely to grow and here the biotransformation route will rule over traditional chemical methods [18].

5.1 Enzymatic Desizing

In the textile industry fabrics made from cotton or blends require coating the warp threads with an adhesive substance known as “size” to lubricate and protect the yarn from abrasion and prevent the threads from breaking during weaving. After weaving, the sizing agent and natural noncellulosic materials present in the cotton must be removed in order to prepare the fabric for dyeing and finishing. Amylase is a hydrolytic enzyme that catalyzes the breakdown of starch to sugars, dextrin, and maltose. An amylase enzyme can be used for desizing processes at low temperature (30–60 °C) and optimum pH is 5.5–6.5. The enzyme is starch specific and does not affect the other components of the fabric [65].

Although many compounds have been used to size fabrics, starch and its derivatives are commonly used owing to good film-forming capacity, availability, and relatively low cost. After weaving the size and natural noncellulosic materials present in the cotton are removed to make the fabric suitable for the following processes such as dyeing and finishing. Desizing used to be carried out by treating the fabric with acid, alkali, or oxidizing agents at high temperatures but the process was not effective in total removal of starch causing imperfections in dyeing and degradation of the cotton fiber. Amylases are commercialized and used extensively in pretreatment due to many advantages including high efficiency and specificity, and complete removal of the size without any harmful effects on the fabric. The starch is randomly cleaved into water-soluble dextrins to be removed by washing. The added benefits were reduction of the discharge of waste chemicals as effluent and improved working conditions [66].

5.2 Bioscouring

The use of pectinases as agents for scouring cotton was quite popular but much research was focused on optimization of the conditions of their activity. Many conditions were important in the performance of the enzymes such as concentration of the enzymes in the bath, time and temperature of treatment, pH of the bath, additives, and the mechanical treatment. In addition to the above, the pH of the environment is crucial for the activity and stability of the enzyme which ranges between 5 and 9. An alkaline or acidic environment depends on the type of pectinases. Acidic pectinases function in a slightly acidic medium (pH between 4 and 6) and alkaline pectinases function in a slightly alkaline medium (pH between 7 and 9). In acidic medium the pectin structure degrades without adding the pectinases which results in better functioning of the acidic pectinases over the alkaline pectinases. Care must be taken to monitor the pH as extreme values lead to the three-dimensional form of the enzymes collapsing and the enzymes losing their catalytic behavior.

A nonionic surfactant and a sequestering agent help in the smooth functioning of the scouring process. Pectin acts as a type of cement or glue that stabilizes the primary cell of the cotton fibers. During scouring with enzymes, a complex is formed between the pectinase and the pectin that causes the hydrolysis of the pectin substances leading to the hydrolysis of the pectin substances. The result of hydrolysis is a split of the bond between the cuticle and the cellulose body. The outer layers are destabilized and removed in the following procedures of rinsing. The enzymes are released to bond again with the pectin. The procedure is continuously repeated until the enzyme is destroyed chemically, with the change in pH or in the temperature. Removal of pectin and other noncellulose substances results in softer fibers with a low whiteness index when compared to conventionally scoured cotton with enzymes inasmuch as seed-coat fragments are not completely removed. Advantages such as a higher quality of the fibers which are softer to touch, better strength, less wastewater, economy of energy, and compatibility with other procedures, equipment, and materials has made enzyme scouring commercially suitable for the industry.

Bioscouring is simple, repeatable, and safe and can be recommended as a standard procedure to the textile industry. The removal of pectin and noncellulosic components from cotton improves the water absorbency of the fibers and helps in the penetration of the dye and other substances into the fiber. Bioscouring can also be used for blends of cotton and silk, wool, and cashmere as the fibers are less damaged. The effluent is less harmful as the load is comparatively lower than the conventional sodium hydroxide scouring pretreatment which results in a highly toxic effluent [18, 67].

5.3 Biobleaching and Biobleach Cleanup

Scouring is regularly followed by a bleaching process, which removes the natural coloration of cotton fibers. Cellulose fibers are bleached with hydrogen peroxide (HP) resulting in high uniform degrees of whiteness and increased water absorbency. However, during the decomposition of hydrogen peroxide, radicals formed cause damage to the fibers. For this reason, organic and inorganic stabilizers and chelators are added to the treatment bath. Hydrogen peroxide (redox potential is 1.78 eV) (1) is ecologically friendly but the large amount of water used to rinse and neutralize the alkaline scoured and peroxide-bleached textiles is ecologically disputable. The bleaching process is conducted in an alkaline bath at pH 10–12 and at temperatures ranging from 90 to 120 °C. Due to the high working temperature, a large amount of energy is consumed. Auxiliary chemicals added into the bath increase the TOC and COD values of effluents. On neutralization of the alkaline waste baths, large amounts of salts are produced. Consequently, the textile industry is considered one of the biggest water, energy, and chemical consumers. Enzymes such as glucose oxidases produce hydrogen peroxide in water solutions in the presence of glucose from oxygen dissolved in water. The degree of whiteness attained in this procedure is lower than the degree of whiteness of the fibers bleached in a classic procedure with hydrogen peroxide. Peracid bleaching can be used as an alternative to hydrogen peroxide bleaching when a medium degree of whiteness is required. Cotton fibers bleached with peracetic acid have good water absorbency, the fibers are not damaged, and the effluent is biodegradable [18].

After the bleaching process peroxide remains in the pretreatment bath and has to be removed before the fabric is to be dyed. The residual peroxide in the bath interacts with the dye molecule and changes the dye shade, causing uneven dyeing. Conventionally, residual peroxide removal has been performed using several sequential rinses with abundant water or by using reducing chemicals such as bisulphite to break the peroxide. The use of a catalase enzyme breaks down hydrogen peroxide into water and molecular oxygen as shown below

$$H_2O_2 + \text{Catalase} \longrightarrow H_2O + O_2$$

The specificity of the catalase enzyme makes the process more sustainable, as no treatment procedure is required .to clean the bath after catalase bleach cleanup is performed. Moreover, there is reliability in peroxide removal ensuring consistency for subsequent dyeing. Savings in total process cost, reductions in water consumption, and wastewater disposal have made the use of catalases one of the most popular enzyme applications in textiles in recent years [53].

5.4 Biofinishing

The use of cellulase enzyme for denim stonewashing and biopolishing of garments and fabrics in the textile industry has been carried out for the past two decades. Initially products were based on the natural ability of certain microbes to degrade cellulose but the growth environment of these microbes showed that a wide variety of proteins are formed that work in several ways to break down cellulose. Modern biotechnology has various tools with which scientists could create new, better enzymes for specific applications. This concept has created a new generation of cellulase products containing different kinds of protein molecules or molecule blends contributing to improved performance features.

Different combinations of the components in cellulase enzyme have been created with biotechnology tools to create new products such as enriching endoglucanase activity, removal of exo-acting cellobiohydrolase activity, or tailoring enzymes with a single type of cellulase molecule. Choosing the right type of enzyme is essential to optimize the cellulose enzyme on a certain fiber type as different fabric types have varying susceptibility for cellulase hydrolysis. Most denim garments are given their worn look using cellulases, either alone or in combination with a reduced amount of stones. The action of cellulases involves loosening the surface fibers of denim for mechanical action in a washing machine which enhances the breaks on the surface to remove the indigo dye to reveal the white core of the ring-dyed yarns. The benefits of this process have been increased washing capacity for the laundries, reduced damage to garments and washing machines, and diminished environmental effects from pumice stone mining and disposal [68].

Table 1 Types of enzymes and their effectiveness against various stains

Enzyme	Effective for
Proteases	Grass, blood, egg, sweat stains
Lipases	Lipstick, butter, salad oil, sauces
Amylases	Spaghetti, custard, chocolate
Cellulases	Color brightening, softening, soil removal

A peach skin treatment involves fibrillation resulting in a soft and smooth fabric surface and biopolishing can be used to clean up the fabric surface prior to a secondary fibrillation process. The peach skin treatment imparts interesting fabric aesthetics and the cellulase enzyme is highly suitable for viscose, modal, and Tencel fabrics. The process time may be 30–40 min and enzyme action is terminated using a high temperature or low pH. A weight loss of 3–5 % is common but reduction in fabric strength can be controlled to within 2–7 %. The entrapment of the fiber residues inside the tubular cotton knitted fabric instead of being washed away is a problem to be addressed [69].

The decolonization of denim has been facilitated by a group of enzymes called laccases, or phenol oxidases. They have the ability to catalyze the oxidation of a wide range of phenolic substances such as indigo dye. Basically laccases are not effective as bleaching agents but require a mediator molecule which is the actual substrate of the laccase. In conjunction with the mediator molecule, laccase helps in the electron transfer from indigo dye to molecular oxygen. Laccase-mediator systems have been used to bleach indigo, enhance abrasion levels, and reduce back staining [66, 68].

5.5 Textile Aftercare and Wastewater Treatment

Enzymes have been used in detergents ever since 1960. This trend has increased drastically and washing powders are referred as "biological" because they contain enzymes. A wide range of enzymes are now available that can degrade many types of stains; their use saves energy and protects the fabric as washing is performed in milder washing conditions at lower temperatures. Some of the major classes of enzymes and their effectiveness against common stains are summarized in Table 1.

The use of advanced granulation technology has addressed the early problems of allergic reactions associated with the use of enzymes. The use of sodium perborate in detergents has been reduced by 25 % and the release of salts into the environment has also been curtailed after enzyme adoption in the detergent formulation process. However, enzymes have to make a corresponding impact upon the commercial laundering market which causes a considerable amount of pollution to environment. High investment costs in continuous-batch systems and tunnel washers cannot accommodate new concept machines. This washing equipment allows a residence time of 6–12 min which is not sufficient to fulfill the adequate performance of the present enzyme systems. Moreover, the methods of enzyme deactivation are not suitable because of the degree of water recycling in modern washers [21].

The extreme conditions of processing have given rise to a popular area of research to investigate enzymes that can tolerate or be activated in hot and cold temperatures. The search for thermotolerant and cryotolerant enzymes has been undertaken as they are desirable for improving laundry processes in hot water cycles and/or at low temperatures for washing colored and dark fabrics. They are also useful for industrial processes where high temperatures are required and for bioremediation under harsh conditions (e.g., arctic).

Technologies using different DNA techniques such as site-directed mutagenesis and DNA shuffling have contributed to form recombinant enzymes that are engineered proteins for special end uses [70].

The degradation of toxic wastes has entered a new perspective through the use of microbes or their enzymes. Color removal from dyehouse effluent and disposal of toxic heavy metal compounds and pentacholorophenol, are some of the hazards facing the textile industry which needs the attention of biotechnologists [16, 71]. Treatment of waste materials and effluent streams from the textile industry has been formulated using natural and enhanced microbial processes. In most cases conventional activated sludge and other systems are generally able to meet BOD and related discharge limits. Synthetic dyes have inherent characters that makes them resistant to microbial degradation under the aerobic conditions. Furthermore, their water solubility and the high molecular weight inhibit permeation through biological cell membranes. The organic contaminants in textile waste are converted to methane and carbon dioxide by anaerobic processes. These processes require less space and treat wastes containing 30,000 mg/l of COD with the benefits of lower running costs and the production of less sludge [21, 72].

Combinations of different enzymatic processes in the same bath will help streamline several processing stages and ultimately result in savings in the usage of time, energy, water, and cost. Some examples are given here.

- Combined bleach clean-up and dyeing: Using catalase enzyme the hydrogen peroxide is first removed, followed by dyeing in the same bath as the enzyme neutralizes the bleach and does not affect the dyes.
- Combined bioscouring and biopolishing: Using two different enzymes with overlapping temperature and pH profiles, one for bioscouring and other for biopolishing have produced a synergistic effect to give better results.
- Combined desizing and bioscouring: The pH and temperature profiles for these two products overlap and this allows for combining the processes of desizing and bioscouring in pad-batch conditions.

There are many problems in the textile industries and with new ecoregulations cropping up, an efficient remedial system is essential to opening new solutions. The focus is on improving the quality of bast fibers such as hemp and linen, wool, and even synthetic fibers; finding alternative ways of dealing with sizing agents other than starch; and evolving methods to break down dyestuffs in the effluents from dye houses and denim-finishing laundries. With this background and the need to move towards sustainable development, biotechnology can help the textile industries by providing useful solutions in the form of specially engineered enzymes tailored to meet the demands of the new process flows and sequences developed for the future goals of clean ecological processing [73].

6 Future Trends

The European federation of biotechnology has reported that to facilitate the technological applications of the potential of microbes and cultured tissue cells the integrated use of biochemistry, microbiology and chemical engineering is essential through biotechnology [21]. Industrial biotechnology is a conglomeration of biology, microbiology, biochemistry, molecular biology, chemistry, process engineering, and so on, and this can be a great strength as combining knowledge from different scientific disciplines can create unexpected results. To achieve innovation and sustainability, projects with members from multidisciplinary fields would help in the development of research. The textile industry, a major contributor to pollution, is a key sector for the application of biotechnology towards sustainability. The awareness is currently very low though the opportunities are high. Novel methods can be adopted in the textile industry for sustenance in the competitive world where eco-friendliness and clean technologies are of primary importance [19].

Some of the advanced techniques of biotechnology suitable for the textile sector are nucleic acid (DNA/RNA)-related technologies, protein/peptide-related technologies, metabolite-related technologies, and cellular and subcellular level related technologies.

6.1 Nucleic Acid (DNA/RNA)-Related Technologies

Sequencing of genome, gene, DNA, DNA synthesis and amplification, genetic engineering, and antisense technology are some of the technologies that come under this group.

- DNA, RNA, gene or genome sequencing is a process for formulating the nucleotide sequence of a DNA/RNA fragment/a gene/whole genome. The entire hereditary information of an organism encoded in the DNA, inclusive of the genes and the noncoding sequences make up the genome. A specific trait, condition, or disease brought through inheritance is due to genes that are definite regions of the genomic sequence. The information from DNA to the protein synthesis sites are encoded and carried by messenger RNA (mRNA). The study of the genome of an organism and the information contained in it, termed genomics, will help in understanding and manipulation of the genes. The study of the expression level of genes is called transcriptomics, measured either in one set of all mRNA molecules or in a cluster of biological cells for a specific set of environmental conditions. Toxicity of the cotton seed in the species Gossipium australe is due to the production of a harmful substance called gossypol. Tao et al. have reported that the transcriptome sequencing, differential gene expression analysis, and delayed gland morphognesis of the above variety of cotton has produced seeds with less gossypol making it less toxic [31].

- DNA sequencing involves the identification of genome structures called genomics mapping, the comparative analysis of gene sequences in order to find similar sequences and the prediction of protein structures. One of the main tools for high-throughput whole genome sequencing is microarrays. A DNA microarray is produced by using cellular mRNA to make segments of the complementary DNA. The complementary DNA (cDNA) segments are attached to a nylon or glass surface at known regions to hybridize into a sample DNA.
- DNA synthesis and amplification. The technique of reproducing a known sequence of nucleotides into genes or gene fragments through polymerase chain reaction (PCR) is called DNA synthesis. DNA amplification is the duplication of DNA sequences and is used to detect very small amounts of DNA. Specific techniques are used for the identification of individuals and for distinguishing between individuals of the same species using only samples of their DNA by genetic fingerprinting or genotyping. All these techniques will be able to identify the DNA in raw material which will help to improve the properties and also give more benefits to the manufacturers and textile industries whose process parameters are based on raw materials. In a patented study, DNA was extracted from a mature cotton fiber sample and subjected to polymerase chain reaction techniques that enable the identification of a particular cotton species utilized in the textile or cotton material of interest [30]. As each individual has a specific DNA profile, the PCR technique will be a good identification tool that will be useful in plant and animal breeding. Genes with significant effects can be specifically targeted in selection and detected by genome mapping.
- Antisense technology prevents the transcription of a DNA using antisense mRNA. The DNA is double stranded and when transcription takes place the sense strand of the DNA produces mRNA. The complementary strand of the DNA is termed antisense. Antisense mRNA is a RNA strand complementary in sequence to the mRNA. The presence of an antisense mRNA can inhibit gene expression by base-pairing with the specific mRNAs. This concept is used to assess the gene function of the particular gene by adding its antisense mRNA transcript. Raemakers et al. have reported the development of amylose-free improved cassava starch by antisense inhibition of granule-bound starch. This starch with improved functionalities is used for paper and textile manufacturing [55].

- Genetic engineering is a specialized tool in biotechnology that modifies organisms to optimize production of existing or new metabolites of industrial importance and for transferring genetic material called genes from one organism to another. An understanding of the responsibility of the genes in determining the characteristics and properties of a living organism and methods of isolating the DNA which carries the genetic code to manipulate them outside the cell, has given rise to new developments in tailoring properties into organisms. The next step would be to introduce fragments of DNA obtained from one organism into another, to transfer some of the properties of the first to the second. For example, scientists working for the leading enzyme producer, Novo of Denmark, discovered that an enzyme produced in minute quantities by one particular fungus had very desirable properties for dissolving fats. The relevant genes were spliced into another microorganism that was capable of producing the desired enzyme at much higher yield. The methods used in genetic engineering for the production and modification of textile fibers have been under extensive study. One approach in genetic engineering systems is to produce monomeric protein molecules in solution from appropriately engineered genes. These can be manifested in bacteria, cell cultures, or in the milk of transgenic animals such as goats or sheep. The protein monomers are then isolated from the system and may be spun or drawn into fibers. The other approach is to modify keratin fibers such as wool by expressing other proteins in the internal components by trangenesis. The fiber obtained from the animals such as sheep will have new and modified properties as per the features exhibited by the transgenes.

6.2 Protein-Related Technologies

High-throughput protein/peptide identification, quantification and sequencing, protein/peptide synthesis, and protein engineering and biocatalysis are some of the protein-related technologies that can be used in the field of textiles. High-throughput protein identification, quantification, and sequencing use a number of techniques that help proteomics which is the study of the structure and function of proteins. The techniques include two-dimensional gel electrophoresis, mass spectroscopy, and nuclear magnetic resonance. The methods used to separate, identify, and quantify levels of proteins and peptides in a mixture are known as gel-electrophoresis (GE). Telke et al. have stated that using sodium dodecyl sulfate polyacrylamide gel electrophoresis purified laccase enzyme with 66 kDa was obtained. The purified enzyme decolorized structurally different azo dyes with variable decolorization rates and efficiencies ranging from 68 to 90 % [56]. For the identification of proteins or other macromolecules through their molecular weights (mass) and to determine the composition and order of amino acids, called sequencing of protein molecules, mass spectroscopy (MS) is used. First the protein molecules are separated through gel electrophoresis followed by alkylation and breakdown in specifically known ways using enzymes into peptides. The third technique nuclear magnetic resonance (NMR) is used to describe the three-dimensional structure of proteins, peptides, and other macromolecules.

Peptide synthesis is another technology where the chemical construction of a known protein or peptide molecule is studied by solid-phase synthesis. Here molecules are bound to a bead and created step by step in a reactant solution with constituent amino acids repetitively coupled to a growing polypeptide backbone. This backbone is attached to a substrate or polymeric support. Automated synthesizers are useful to synthesize proteins in this manner.

Protein engineering and biocatalysis: In industrial production processes and in bioremediation applications, enzymes are engineered by the selective, deliberate design and synthesis of proteins in order to alter specific functions. This process is known as protein engineering. Biocatalysis is the use of enzymes as catalysts to perform transformations in organic compounds. Enzymes for protein engineering and biocatalysis can be used in isolated form, or inside living cell lines, or as microorganisms such as bacteria, fungi, and yeasts. There are two general strategies for protein engineering. One strategy involves the use of detailed knowledge of the structure and function of the protein to make desired changes termed rational design. The second strategy is random mutagenesis such as DNA shuffling applied to a gene and a selection system used to pick out variants that have the desired qualities called directed evolution. DNA shuffling involves taking a set of closely related DNA sequences, segmenting them randomly, and reassembling the fragments into genes. A combination of positive or desired mutations can be rapidly formed and the output of this cycle will form the input of the next cycle. This systemic DNA shuffling leads to directed evolution and can be applied to evolve any protein rapidly although the structure or the catalytic mechanism is unknown [60].

6.3 Metabolite-Related Technologies

These include high-throughput metabolite identification and quantification and metabolic pathway engineering. Molecules that are the intermediates and products of metabolism are called metabolites. They are the end product of the gene expression process and are involved in the normal growth, development, and reproduction of living organisms.

- High-throughput technologies for identification, quantification, and analysis: MS and NMR are the two leading technologies for metabolomics. MS is used to identify and to quantify metabolites after separation. The mostly commonly used separation technology is gas chromatography in combination with MS.
- Metabolic pathway engineering: Metabolic pathway engineering includes the modification of endogenous metabolic pathways of microorganisms and the

introduction of metabolic pathways into new host organisms. In addition, metabolic engineering also deals with the upregulation of the production of molecules. It is one of the most important tools in industrial biotechnology. John and Keller state that *Alcaligenes eutrophus* genes encoding the enzymes, β-ketothiolase (*phaA*), acetoacetyl-CoA reductase(*phaB*), and polyhydroxyalkanoate synthase (*phaC*) catalyze the production of aliphatic polyester poly-*D*-(–)-3-hydroxy-butyrate (PHB) from acetyl-CoA. Transgenic cotton fibers were produced by particle bombardment of (*phaB*) and (*phaC*) genes. The presence of PHB in the transgenic cotton fibers resulted in measurable changes in thermal properties [57].

Metabolic pathway engineering encompasses a combination of technologies, including those used in genomics and proteomics studies, genetic engineering, and so on. The metabolism of microorganisms is engineered in order to improve their suitability for biotechnical processes and for efficient production of many sorts of chemical compounds.

6.4 Cellular and Subcellular Level-Related Technologies

These technologies include cell hybridization/fusion, hybridoma technique, cell and tissue culture and engineering, and embryo technology.

6.4.1 Cell Hybridization/Fusion

When the cell contents of two or more cells of different species origin combine, in vitro, into a single cell, it is known as cell fusion. The nucleus of the donors may either remain separate or fuse together, but the following cell divisions would have a single spindle so that the new cell has a single nucleus containing complete or partial sets of chromosomes from each parent.

6.4.2 The Hybridoma Technique

Here cell fusion techniques are used for the production of monoclonal antibodies. The product of fusion is called hybridoma which is a synthetic hybrid cell. The monoclonal antibodies are often used in immunoassays as they usually bind to only one site of a particular molecule. The monoclonal antibodies produced by hybridoma react on a single antigenic determinant of an antigen. On the basis of the reaction of an antibody to its antigen, an immunoassay measures the level of a substance in a biological liquid. Monoclonal antibodies serve as a specific and accurate biochemical test that measures both presence of antigen or antibodies.

6.4.3 Cell and Tissue Culture and Engineering

The mainstream technologies under cell culture technologies are the in vitro growth of cells isolated from multicellular organisms. These technologies vary for plant cell cultures and for animal and human cell cultures. The in vitro growth and/or regeneration of plant material under controlled conditions is called micropropagation. Tissue engineering is a more advanced culture technique where specific animal or human cells are induced to grow and form entire tissues that can be implanted in the human body. Another method is to inject relevant compounds such as growth factors or growth hormones or living cells into the body to grow and form desired tissues. To develop biological alternatives that restore, maintain, or improve tissue function, tissue engineering uses a combination of cells, engineering materials, and biochemical factors. The required cells are embedded into the scaffolds which are artificial structures that promote three-dimensional tissue formation. The seed cells can come from the same body to which they will be reimplanted, from another body, or even from other species. Ing et al. have mentioned the contributions made by researchers for the development of innovative resorbable porous scaffolds for tissue engineering and regenerative medicine [74].

6.4.4 Embryo Technology

Embryo technology involves the removal of an embryo from a donor and immediately transferring it to a surrogate mother. This technology may be more complicated and advanced by performing microsurgery on the embryo and maintaining the embryo in special culture systems before transferring the embryo to the surrogate mother which may be in vivo and in vitro embryo production. Embryo technologies are being adapted to livestock as embryo transfer, embryo splitting, and cloning. In embryo transfer, animal embryos are transferred to recipients via artificial inembryonation. Embryo splitting is the splitting of young embryos into several sections; each section develops into an animal that is genetically identical to the others. Cloning involves the asexual processes of creating an identical genetic copy of the original organism without the interchange or combination of genetic material. The members of the clone have genetic compositions that are identical. It has been reported that Dr. Shah, a pashmina goat cloning pioneer had made interesting reflections of his work at the Cashmere World 2012 conference [74]. In the production of embryonic stem cells, the new egg is stimulated to start dividing to form a blastocyst after which embryonic stem cells are harvested. These embryonic stem cells are employed to generate chimeric animals. Chimeric animals are animals whose cells are not all genetically identical, which may be due to somatic mutation, grafting, or because the individual is derived from two or more embryos or zygotes. These are further used to produce knockout animals that are used mainly in research. Apomixis is associated with cloning used in plants. Here the plant seeds are genetically identical to the parent plant as biological reproduction is done without fertilization.

6.5 Fermentation and Downstream Processing

The anaerobic breakdown of complex organic substances such as carbohydrates, by microorganisms to yield energy is fermentation. In the industry fermentation is the term used for aerobic, anaerobic, microaerofilic culturing of defined microorganisms and the culturing of mammalian and insect cells. In a fermenter or bioreactor, organisms, cells, cell extracts, or biochemically active substances derived from organisms act on complex organic substances. After the fermentation process is completed, a large quantity of a dilute mixture of substances, products, and microorganisms is produced. These products must be separated in a controlled way and the product should be concentrated, purified, and converted into a useful form. This process is called downstream processing. A bioreactor is a device or system to grow cells or tissues in culture as in tissue engineering. They are commonly cylindrical and made of stainless steel, ranging in size from a liter to several cubic meters. A variety of products is produced through fermentation including biomass, primary and secondary metabolites, bioconversion products, enzymes, and recombinant products which are used in many biological and industrial applications. The separation and purification of the products to make them suitable for the required end use is the work of downstream processing. These two processes go hand in hand to produce new and unique products that are biologically friendly to the environment.

6.6 Bioinformatics

Bioinformatics is the creation, collection, storage, and efficient use of data and information from all fields of biotechnology and combinatorial chemistry research. Examples of the data that are manipulated and stored include gene sequences, biological activity or function, pharmacological activity, biological structure, molecular structure, protein–protein interactions, and gene expression products, amounts, and timing. Major research efforts in the field include sequence alignment, gene finding, genome assembly, protein structure alignment, protein structure prediction, prediction of gene expression and protein–protein interactions, and the modeling of evolution. The terms “bioinformatics” and “computational biology” are often used interchangeably. Bioinformatics is the database loaded with information whereas computational biology deals with algorithm development and specific computational methods.

There are many challenges confronting biotechnology while focusing on textile applications. The specific key areas that requires special attention are as follows.

- Synthetic biology and metabolic pathway engineering are examples of emerging technologies that will significantly increase the diversity of biotechnological processes and products, driving the development of innovative products.
- Some biobased products will require further chemical processing and unless these chemical processes are made available there will be no market for these precursors. Therefore dedicated research on the combination of technologies such as biochemical and chemical processes should be undertaken.
- Another important field is the development of efficient and robust enzymes, particularly for the conversion of lignocellulosic material. This should enable the conversion of a variety of feedstock.
- Specific research is also needed to improve feedstock yield and/or the composition of biomass involving both plant genomics and new breeding programs, and also incorporating further research into efficient crop rotation, land management and land-use change issues [75].

In order to make a fast and efficient shift towards more integrated and sustainable production and processing systems, many measures are to be taken. Attention should be to extend support of technological progress and increase public and private R&D investment in industrial biotechnology and related technologies, through multidisciplinary research programs at both the national and international levels. Efforts need to be made to build networks between industry and academia to overcome the competence hurdle and knowledge gap to stimulate and support technology transfer in the area of industrial biotechnology and green technologies. Sufficient resources must be mobilized to support large coordinated research initiatives, focusing on the market perspective covering the whole value chain. Programs to accelerate and alleviate risks of transforming knowledge into commercial products, by financially supporting access to pilot and demonstration facilities and by integrating production processes need to be established.

7 Conclusion

A product is sustainable only when all the input and output parameters of materials and processes are harmless to living beings and the environment in all stages of the product lifecycle. Renewable and recyclable sources are essential for energy, material, and process inputs. It also means that the products manufactured must be capable of returning safely to their natural or industrial systems in all stages of the product lifecycle to ensure social well-being, health, and safety. Sustainability in the field of textiles can be attained by the use of biotechnology as all the techniques and processes are biologically safe and natural.

The main culprits of pollution in textile and apparel production are water, energy and chemical use, and pollution. The factors for sustainable production are to be reviewed from the raw material to the finished product in terms of selection, sourcing, manufacture packaging and supply, warehousing, and retailing. Once the product is used and worn its impact on the environment is also accountable. In all stages of the product lifecycle researchers, manufacturers, and industrialists must take care to look for sustainable solutions to overcome the problems facing the textile industry. Most of the raw materials and energy are from nonrenewable resources and the freshwater supply is becoming scarce. Industries have to take note of the carbon foot print and modify their conventional style of working to start introducing green and clean processes to stay in the competitive market that is globally accessible to all consumers. Sustainability has been extended from environmental issues to social issues and many laws and regulations have been passed to maintain the safety of humans and environment from the hazards of pollution.

Industrial biotechnology would serve to solve many problems faced by the textile industry. Many novel tools and techniques in modern biotechnology can help the industry, such as improving the performance and yield of the raw materials such as textile fibers, wool and silk, creating new materials from renewable natural resources, aiding in the processing of fabrics with enzymes, biological dyes, and improved methods that would save water and fuels and resources for future use. Enzymes in processing would save time, energy, raw materials, water, and cost and would make the entire process viable, sustainable, and eco-friendly. Manipulation of genes and embryos give rise to new combinations for suiting different requirements. Bioremediation methods can also be used for clean-up processes to help in bringing about zero discharge. Thus biotechnology can serve all areas of textiles and create an awareness of the eco-friendly methods to be adopted by the textile industry. Government aid for undertaking research in all areas of biotechnology for textile applications is a prospective need and will help the textile industry to blossom and flourish in a sustainable way for future well-being and happiness.

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Jute-Based Sustainable Agrotextiles, Their Properties and Case Studies

Sanjoy Debnath

Abstract Jute is a natural plant fiber that is produced annually. It has good acceptability in today's world of geotextiles and agrotextiles for sustainable development. Its unique eco-friendliness adds to sustainable growth of the agrotextile arena. Recently many approaches have been made wherein jute is being used in different forms in the area of agriculture apart from its conventional applications. In this chapter jute-based agrotextiles, their properties and some important case studies have been showcased for sustainable eco-friendly agricultural applications after prolonged use. The natural degradation of the jute-based material with soil, enriches fertility of the soil apart from its unique behavior during its service life. Hence, this sustainability of soil health using jute-based agrotextiles is another important aspect apart from its conventional plastic material application in agriculture.

1 Introduction

Jute cultivation in India is one of the oldest cultivated fiber crops and was used in technical [36] applications for more than 1,000 years. In the eastern part of India, jute fiber/stick is used for reinforcement of rural mud houses. It is a well-established fact that even today, some of the farmers are cultivating jute for its sticks which are popularly consumed as fuel for cooking in domestic country ovens. For most of us jute is well known for its use as packaging material of agricultural as well as some industrial products and also as carpet-backing cloth material. Due to its good surface friction and high level of dimensional stability it can retain its shape as well as structure during transportation when used in the case of packaging

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material. Due to its nature-friendliness and good water-absorbing property [19] it is suitable for sustainable agricultural applications. Application of jute in agricultural can be made more effective in its different forms viz., fiber, yarn, rope, fabric, and nets [12].

1.1 Types of Jute-Based Agrotextiles

In the field of agriculture different textile materials have been used since ancient days. The agrotextile materials may be categorized as per the applications: with soil, as packaging materials for agricultural products, for cattle, for plants and trees, and for cannel lining. Among these, in the present chapter emphasis is made on the application of jute-based textile material suitable for agricultural soil application. Under this broad classification, agricultural mulch, riverbank protection, and cannel lining are some of the major areas discussed.

1.2 Studies of Mechanical and Hydraulic Properties of Jute Geotextile for Agrotextile Applications

The role of jute agrotextiles in the majority of its applications is biotechnical [3] areas. In the case of geotextiles, except in strengthening of roads, its objectives are improvement of soil properties and growth of vegetation on it. In the irrigation in agricultural fields, protection of river/canal banks, jute-geotextiles/agrotextiles can easily replace the conventional granular filter made up of varying grades of coarse aggregates. Vegetation growth on geotextiles/agrotextiles on its biodegradation slows down the intensity of current hugging the bank. In the present study efforts have been made to determine the concerned mechanohydraulic properties of jute-geotextile/agrotextile wherein air and water permeability matter the most [10]. It is evident from the results that considering the strength parameter, woven jute-geotextiles/agrotextiles perform better in geotechnical applications and nonwoven jute fabrics that show lower permeability and higher water retention characteristics may find favor in applications where separation and drainage functions are to be performed.

1.3 Mechanical Properties of Geo/Agrotextile Material

Mechanical properties of jute geotextiles are basically indication of the product's resistance to mechanical stress developed as a result of application of loads and installation conditions. Depending on the application, geotextiles must be able to bear a load or to undergo deformation. A load will cause deformation but also a deformation will mobilize a tension in the geotextile. The relationship between load and deformation can, in general sense, be considered as mechanical behavior. Loading can be in the plane but also perpendicular to the plane of the geotextile. In this respect it is important whether the stress is uniformly distributed. In the latter situation, stress concentrations develop that often lead to failure. The maximum stress corresponding to the breaking load is referred to as the tensile stress with the maximum specific stress as the tenacity. The tensile strength is characterized by the modulus of elasticity where tangent modulus means the slope of the tangent at a particular point on the stress–strain curve. A well-known tangent modulus is the initial modulus, which relates to the tangent at the fairly straight part of the stress–strain curve. The secant modulus is the slope of the line between two particular points on the stress–strain curve. A geotextile is not able to bar compression forces in its plane, because both the constituting elements (fiber and yarns) and the geotextile itself are very flexible and tend to buckle by compression. The mechanical properties of a geotextile depend on the mechanical properties of the fiber material and fiber structure, the yarn structure, and structure of the geotextile. Furthermore, the property depends also on the direction because of the anisotropy of the structure [24]. In general, two directions have to be differentiated: warp and weft in the case of woven geotextile and machine direction and cross direction in the case of nonwoven.

In addition to the tensile tests in which the geotextile is subjected to load and/or displacement, tests can be devised to predict the bending behavior of geotextile fabric. Stiffness is one of the basic mechanical properties and plays a significant role when the fabric comes in contact with the soil to follow the soil surface contours in different practical applications. Stiffness of the geotextile fabric samples can be investigated by examining different bending parameters, for example, flexural rigidity and bending modulus.

1.4 Hydraulic Properties of Geo/Agrotextile Material

Although nonwoven can be produced for jute geotextile applications, woven geotextiles can cater to most of the applications of filtration, separation, and drainage. The nonwoven may prove to be more efficient in agro-plant mulching, weed control, and erosion control applications because of their high water retention and high planar water transmissions. Its low conductivity also assists in keeping the effects of evaporation and conserving moisture. Woven geotextiles promote good surface flow down the slope arresting the direct impact of raindrops on the bare soil whereas the nonwoven underneath discharges absorbed water by in-planar flow down to the toe drains thus inhibiting saturation during monsoons.

Diversified geotextile applications of jute geotextiles include agro-plant mulching where passage of air through the geotextile fabrics is of utmost importance. This application mainly demands air permeability of the jute fabrics, which is the rate of fair flow through a fabric under a differential pressure between the two fabric surfaces. Although this property may only give some indications regarding openness and porosity of the fabric [22], it could be helpful to relate and to analyze other permeability characteristics of the geotextile fabrics. Jute geotextile material provides very beneficial microclimatic conditions for germination and growth of plant life. It also offers a moderating influence on temperature and desiccation. The ability of jute to store water is important and particularly in halter and dry periods, this storage and subsequent releasing of moisture over an extended span of time will maintain the required humidity for a longer time. Thus, a more favorable germination condition may prevail. This phenomenon demands the suitability of the use of jute geotextiles for mulching purposes.

This chapter highlights jute-based material as natural fiber that can serve its technical and functional purposes during its service life, and after degradation it will be a part and parcel of the soil. Application of this jute-based material in agriculture can lead to sustainable agricultural development due to its almost completely positive aspects. Before application of jute-based materials in agricultural application is essential to understand some of the important properties of jute geotextile/agrotextile materials used in agricultural application. In this chapter emphasis is on properties and some important promising application areas of jute textile material used in sustainable agricultural development.

2 Materials and Methods

2.1 Materials

In the present investigation [32], jute geotextile fabrics have been selected with two basic constructions: woven and nonwoven. Fabric area densities of 200, 250, and 300 g/m^2 have been considered for woven fabrics (plain weave), and 150, 200, and 250 g/m^2 for nonwoven construction; in the case of woven fabric, 150 g/m^2 has not been included because its highly porous structure is unsuitable for mulching application. Construction details of the woven fabrics are given in Table 1. These include the thread density in both principal directions of the fabrics (warp and weft), linear density (tex value) of the constitute yarns (warp and weft), and fabric cover factor.

2.2 Methods

Before subjecting the fabrics to evaluation, the samples were conditioned at 65 ± 2 % relative humidity and 27 ± 2 °C temperature for 72 h. The fabrics were tested following ASTM D 5261-92 for evaluation of fabric area density and ASTM D 5199-91 [7] for measurement of thickness. Fabric area density and thickness values are shown in Table 2.

Table 1 Construction details of woven jute geotextile fabrics

Parameters	Woven fabrics		
Area density (g/m^2)	200	250	300
Ends/dm	39	51	55
Picks/dm	39	39	47
Warp count (tex)	264.24	250.59	265.93
Weft count (tex)	238.43	250.50	269.35
Cover factor	11.5	13.0	14.8

Table 2 Physical properties of woven and nonwoven jute geotextile fabrics and plastic material

Parameters	Woven fabrics			Nonwoven fabrics			Plastic
Area density (g/m^2)	200	250	300	150	200	250	50
Thickness under 2 kPa pressure (mm)	1.15	1.05	1.15	1.30	1.56	2.05	0.025

2.2.1 Measurement of Tensile Property

All the samples were tested for tensile strip test on an Instron Universal Tensile Tester (Model-5567) following the standard test method ASTM D1682-64 [1] under standard atmospheric condition (65 ± 2 % relative humidity and 27 ± 2 °C temperature). For woven fabric, the ravel-strip and for nonwoven cut-strip test methods have been conducted. In the case of woven fabric, the specimen width was 50 mm after raveling uniformly from both sides of the sample. For the nonwoven sample the specimen width was selected as 25.4 mm. The gauge length was set at 75 mm for the woven as well as nonwoven samples. The strain rate was set in such a way that the failure of the samples occurred between a timespan of 20 ± 3 s, depending on the type of the fabric samples. Maximum load (in terms of Newton unit), and breaking extension percentage were noted. From the value of breaking load, the tenacity values are calculated by following formulae:

$$\text{Fabric Tenacity (cN/tex)} = \frac{\text{Breaking load (N)}}{\text{Specimen width (mm)} \times \text{ Fabric area density (g/m}^2\text{)}} \times 100$$

The initial modulus and secant modulus have also been calculated from the respective stress–strain curves.

2.2.2 Measurement of Air Permeability

Evaluation of air permeability of both woven and nonwoven fabric samples was conducted, using the Shirley Air Permeability Tester (SDL-21). The results have been expressed as the units of volume of air in cubic centimeters, passed per second, through one square centimeter of fabric at a pressure difference of 10 mm or 1 cm head of water [2]. But in some cases, the range of flow meter available in the instrument may not achieve the high flow rate required for this specific pressure difference. In such a case, superimposed layers of fabric on one another have been tested at a time and the flow rate reading for a single layer was calculated by multiplying the result by the number of layers [35]. Air permeability value was calculated by dividing the flow rate reading in cc/s at 1 cm pressure head of water by the test area, which is in this instrument 5.07 cm^2 (1 inch^2). Sectional air permeability or SAP [35] value was used to compare the permeability of different fabric samples. The SAP value of all the samples were determined from the following formula:

$$\begin{aligned}\text{SAP} &= \text{air permeability value}\left(\text{cm}^3/\text{cm}^3/\text{s}\right)\\ &\quad \times \text{mean thickness (cm) at 2 kPa pressure}\end{aligned}$$

for each sample 10 tests were performed.

2.2.3 Measurement of Bending Property

Stiffness of the geotextile fabric samples was investigated by examining different bending parameters, for example, flexural rigidity, bending modulus, and so on, at 65 ± 2 % relative humidity and 27 ± 2 °C temperature after conditioning the sample for 24 h. The flexural rigidity of the fabric samples was determined by measuring the bending length following the standard cantilever principle by using the stiffness tester. The average value was calculated from 10 specimens in both warp and weft directions of the woven fabrics. Similarly for nonwoven samples both machine and cross-directions of the fabric specimens were considered. The specimen size of each sample was $150 \times 25\ \text{mm}^2$. The bending length was measured directly from the instrument. Flexural rigidity was calculated from the following formula [8].

$$\text{Flexural rigidity in Newton cm (G)} = \frac{\text{WC}^3}{10^4} \times 9.81$$

where, W = fabric area density (g/m^2); c = bending length in cm.

For the bending modulus, the thickness of each sample was measured under the pressure of 1 lb/in^2 by using the thickness tester (ASTM D5199-91). The bending modulus of the samples was determined from the following formula:

$$\text{Bending modulus in Newton/cm}^2 = \frac{12\text{G}}{\text{g}^3}$$

where, g = thickness (cm) of sample at 1 lb/in^2.

2.2.4 Measurement of Water Imbibation Property

For the measurement of water retention characteristics, the samples were cut into equal sizes of $4 \times 4\ \text{cm}^2$ and weight under the following natural atmospheric conditions.

Dry bulb temperature: 87 °F, wet bulb temperature: 81 °F and relative humidity 77 %

The samples were soaked under distilled water for about 48 h. Later, all these samples were hung in free air for about 40 min to drip out the excess water absorbed by the samples. These samples were kept on a blotting paper for 5 min to absorb further excess water present on the surface of the samples. Now, the weight of the wet samples was taken to find the absorbency of water by using the following formula:

$$\text{Water absorbency}\,(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

Release of moisture with respect to time was determined for all sample units; they achieved the constant weight.

2.2.5 Evaluation of Soil Moisture

The soil moisture or moisture barrier property has been studied under two methods: noncontact method and contact method [4].

2.2.6 Noncontact Method

Seven 100 ml beakers were taken containing 25 ml of water in each beaker. Among them, the mouths of six beakers were tightly covered with the fabric samples and the remaining one was kept as control without any fabric cover. These beakers containing water and samples were weighed initially and weights were repeatedly taken at certain time intervals until they reached a constant weight. This experiment was conducted under normal atmospheric conditions. At each time interval, the percentage of evaporation loss was calculated from the weight difference of the individual beaker assembly at that point of time with respect to its initial weight. The results were plotted as a time versus cumulative evaporation loss to compare the performance of various geotextile fabrics of different fabric weight (Fig. 9).

2.2.7 Contact Method

In this test, seven similar size petri dishes were taken containing 90 gm of standard alluvial soil with saturated moisture in each petri dish. The six petri dishes were covered with fabric samples in such a way that the fabric had direct contact with the moist soil. The control dish was not covered with any sample fabric. To determine the moisture barrier property, the weight of each dish with soil and sample was measured initially. These weights were further taken at certain time intervals until all the dishes reached a constant weight. The cumulative evaporation loss was calculated in a similar method to that of the noncontact process. The results were plotted as a time versus cumulative evaporation loss to compare the performance of various geotextile fabrics of different fabric weight (Fig. 10). This experiment was replicated five times and an average of five readings for each sample was calculated.

2.2.8 Evaluation of Soil Temperature

In this test, selected fabric samples of woven (200 and 300 g/m^2), nonwoven (200 and 250 g/m^2), and commercial mulch material (i.e., black polyethylene sheet, 50 g/m^2 and thickness 25 μm) were evaluated to determine soil temperature behavior with respect to time against control [5].

Six earthen pots of the same size and shape were taken and the same quantity of alluvial soil was filled in each pot. The same quantity of water was poured in all the pots till saturation levels were attained and excess water was poured out. Under this condition, the surface water was allowed to evaporate for 24 h, so that same ambient conditions were attained in all the pots. Woven jute agrotextile of 200 and 300 g/m^2, nonwoven of 200 and 250 g/m^2, and commercial black plastic (polyethylene) sheet of 50 g/m^2 were laid on the top of the soil in each pot. Utmost care was taken to see to it that no part of the soil surface was left exposed/uncovered by the agrotextile/experimental materials. Before covering with the mulching materials, the soil temperature was measured in each pot. The temperature was measured approximately 2.54 cm below the soil surface at five different spots and averaged to determine the mean temperature. Soil temperatures were determined identically as above at a fixed interval of 2 h. This study was continued for four days and temperature recorded for all six pots including control and represented graphically in Fig. 3.

3 Results and Discussion

3.1 Effect of Fabric Area Density on Tensile Property

The experimental results of the tensile parameters are presented in Figs. 1, 2, 3 and 4. A general observation has been found that the nonwoven fabrics show higher extension with poor strength compared to woven fabric. Among the nonwoven samples, the strength obtained at cross-direction was higher than that obtained at the machine-direction of the fabric apparently due to cross-laying of the fibrous web prior to [15] needling. Poor initial modulus and secant modulus have been observed in the case of nonwoven fabrics in comparison to woven fabric irrespective of the direction of the fabric [11]. This may be because twist in the constitute yarns reduces fiber-to-fiber slippage resulting in higher realization of strength in the case of woven fabrics. But in the case of nonwoven fabric, the entanglement of fibers is not so strong which can reduce the fiber-to-fiber slippage during tensile deformation. However, for application in mulching, the initial and secant modulus will not affect the performance of the fabric significantly.

3.2 Effect of Fabric Area Density Versus Air Permeability

The experimental results of air permeability and sectional air permeability presented in Figs. 5 and 6 indicate that the air permeability value drops down with the increase of fabric weight for both woven and nonwoven samples. It may be because the fabric samples attain a more compact structure with the increase in their fabric weight in both cases resisting the airflow through them. It has been found that at 200 and 250 g/m^2 fabric weight the nonwoven shows lesser air-permeability value than that of the woven fabric. Sectional air permeability also shows the same trend. This behavior is due to the lesser porosity and higher thickness of nonwoven fabrics.

3.3 Effect of Fabric Area Density Versus Bending Property

The average values of bending length, flexural rigidity, and bending modulus are presented in Figs. 7 and 8.

In the case of woven fabric, the bending length, flexural rigidity, and bending modulus are found to be higher in the warp direction than in the weft direction, whereas for nonwoven these parameters show higher value in the cross direction than in the machine direction. This is apparently due to the higher thread density in the warp direction in the case of woven samples and higher orientation of fibers in the cross-direction in the case of nonwoven samples. Rigidity values are found to

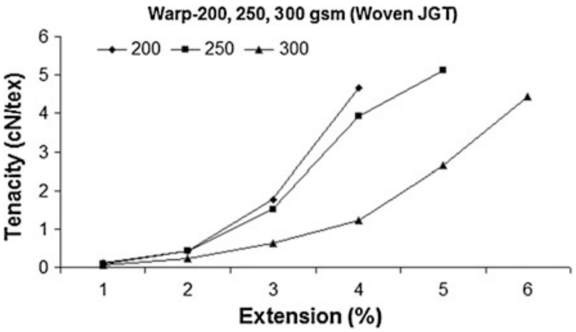


Fig. 1 Tenacity versus extension curve of woven fabric samples (*warp* direction)

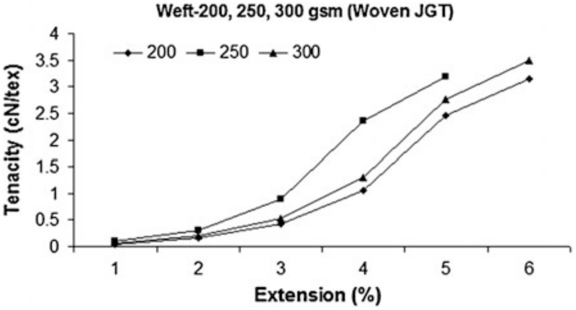


Fig. 2 Tenacity versus extension curve of woven fabric samples (*weft* direction)

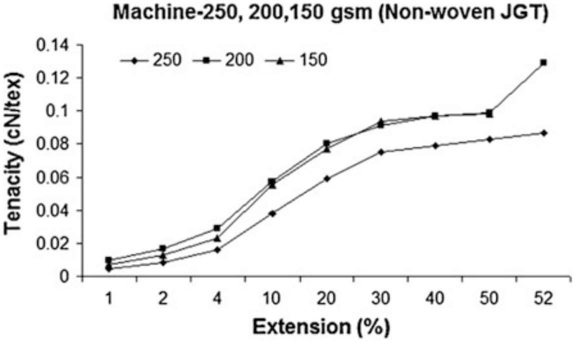


Fig. 3 Tenacity versus extension curve of nonwoven fabric samples (*machine* direction)

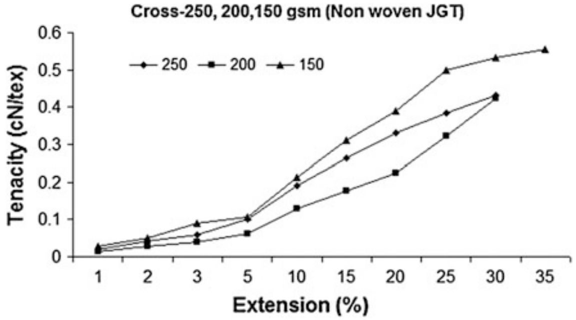


Fig. 4 Tenacity versus extension curve of nonwoven fabric samples (*cross* direction)

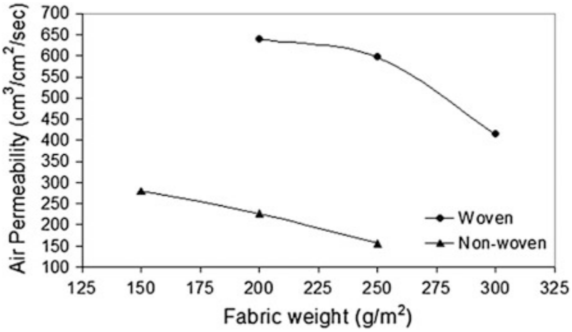


Fig. 5 Effect of fabric weight on air permeability

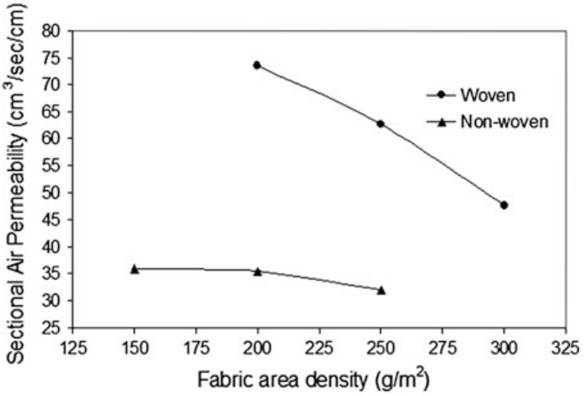


Fig. 6 Effect of fabric weight on sectional air permeability

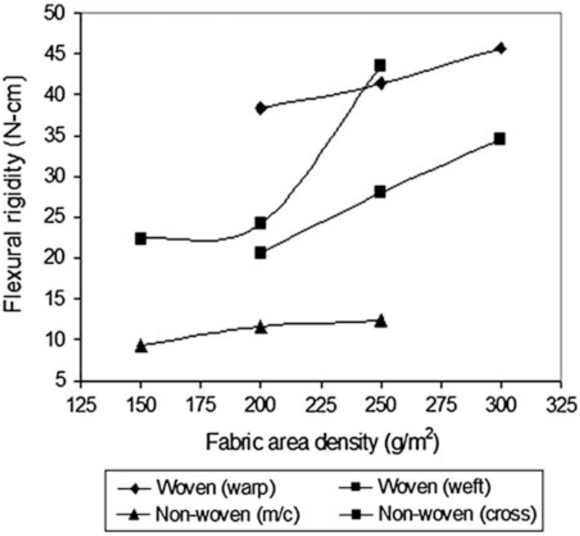


Fig. 7 Effect of fabric area density on flexural rigidity

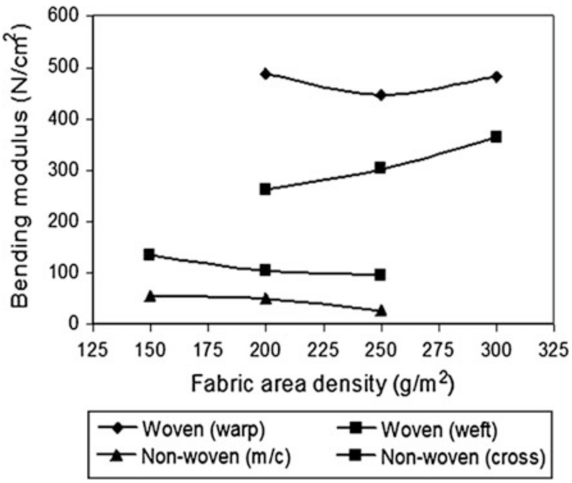


Fig. 8 Effect of fabric area density on bending modulus

be increased with increase in fabric area density for both types of samples at any direction. The thickness of the nonwoven fabrics is considerably higher than that of the woven fabrics due to their inherent bulky structure. This may reflect the lower bending modulus for nonwoven samples than the woven samples irrespective of the fabric area density.

3.4 *Effect of Fabric Area Density Versus Water Retention Property with Time*

The observations on the water retention property with time are recorded in Tables 3 and 4 for woven and nonwoven fabric samples, respectively. It is evident from the results that the water-holding percentage of the nonwoven fabric sample is considerably higher than woven fabric samples. This is because the number of pores present in the nonwoven is considerably higher due to its inherent structure. And also the nonwoven is more voluminous than the woven samples because of its higher thickness. Furthermore, the change of water retention capacity with respect to time has been examined. This result can be correlated from the air-permeability studies. Nonwoven can retain more moisture with the progress of time, sustaining due to its less permeable structure than the woven samples for the same level of fabric weight under study (e.g., 200 and 250 g/m^2).

Table 3 Water retention properties of woven fabric samples

Sample size			4×4 cm^2					
Fabric type			Woven					
Fabric weight (g/m^2)			200		250		300	
Sample weight (g)			0.342					
Water retention properties			Water in gms	%	Water in gms	%	Water in gms	%
TIME	1st Day	At start	0.717	209.65	0.885	240.65	0.973	243.25
		After 30 min	0.635	185.67	0.809	219.24	0.893	223.75
		After 60 min	0.525	153.51	0.712	192.95	0.795	198.75
		After 90 min	0.433	126.61	0.612	168.29	0.702	175.50
		After 120 min	0.322	94.15	0.522	141.46	0.598	149.50
		After 180 min	0.145	42.40	0.339	91.87	0.401	100.25
	2nd Day	After 180 min	0.00	0.00	0.031	8.40	0.049	12.25
		After 180 min	–	–	0.00	0.00	0.00	0.00
	3rd Day	After 180 min	–	–	–	–	–	–

Table 4 Water retention properties of nonwoven fabric samples

Sample size			4×4 cm^2					
Fabric type			Nonwoven					
Fabric weight (g/m^2)			150		200		250	
Sample weight (g)			0.236		0.255		0.283	
Water retention properties			Water in gms	%	Water in gms	%	Water in gms	%
TIME	1st Day	At start	1.818	707.34	2.150	843.14	2.672	944.17
		After 30 min	1.617	685.17	2.022	792.94	2.553	902.12
		After 60 min	1.563	662.29	1.897	743.92	2.424	856.54
		After 90 min	1.404	594.92	1.720	674.51	2.257	797.53
		After 120 min	1.222	517.80	1.534	601.57	2.067	730.39
		After 180 min	1.004	425.42	1.307	512.55	1.846	652.30
	2nd Day	After 180 min	0.017	7.20	0.020	7.84	0.027	9.54
		After 180 min	0.00	0.00	0.006	2.35	0.010	3.53
	3rd Day	After 180 min	–	–	0.00	0.00	0.00	0.00

3.5 Control of Soil Moisture and Temperature by Light-Weight Jute Fabrics

Jute as an annually renewable agricultural fiber has enormous potential to be used not only as conventional packaging material but also as a means to enhance agricultural production as an agro-mulch cover. Jute is hydrophilic in nature.

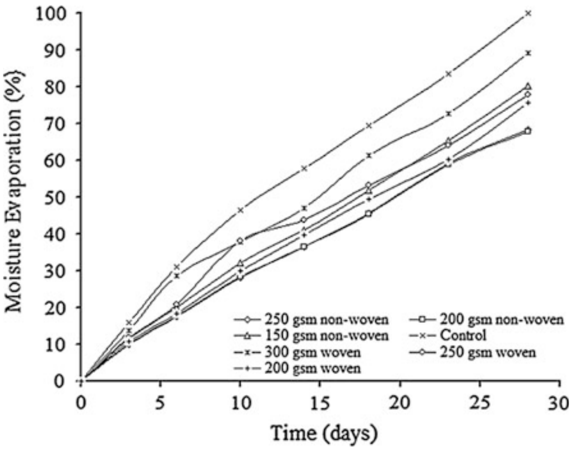
Basically, woven and nonwoven are the two main types of jute fabrics available on the market with a wide range of fabric weights ranging from 150 to 550 g/m^2 or even higher. The needle-punched jute nonwoven has certain advantages over woven jute fabrics in moisture absorption, controlling soil temperature, and the like. In the present studies, attempts have been made to determine the moisture evaporation characteristics of these jute fabrics as well as soil temperature behavior when used as mulch material. The study shows that the nonwoven can restrict moisture evaporation from the soil surface and control the soil temperature more sustainably as compared to woven jute fabrics.

Jute has an inherent characteristic to hold moisture in it and release it gradually in a lengthy spell. Nonwoven fabric made out of jute has normally higher thickness with a large number of small pores as compared to that of woven fabric. Due to its bulky nature, nonwoven also acts as good thermal insulating material [13, 14, 16]. It has been reported that the soil temperature beyond 30 °C showed a decline on root growth of grape root [40]. Researchers [28] at the Coweeta Hydrologic Laboratory in the southern Appalachians also examined and concluded that soil temperature and temperature–moisture interactions significantly affected net soil nitrogen mineralization rates (N_{min}). The conventional mulch material used in agricultural application is black polyethylene, which neither allows sunlight to penetrate through the soil surface nor allows the soil moisture to evaporate easily and ultimately increases the soil temperature in spite of weed control. However, nonwoven jute plays an important role in maintaining the soil temperature due to its higher thickness or bulk. Moreover, jute being an annually renewable agricultural product loses its strength within a period of 3–8 months depending upon the fabric weight and ultimately degrades over a period of time to act as manure to the soil. Due to its bulky structure, nonwoven contains a large number of pores or voids, which can hold moisture for a long duration compared to woven fabrics of same fabric weight [16, 17]. In the present study, two methods of measuring moisture evaporation, that is, the contact method and noncontact method, have been discussed. In field application, some portion of the mulch material comes in close contact with the soil and somewhere there is a gap between the soil and mulch material. Thus the behavior of moisture evaporation may act differently in both the contact and noncontact areas. So, to understand the true nature of moisture evaporation under contact and noncontact conditions, this experiment has been taken up. Another aspect of the jute agrotextile mulch material is to control and sustain the soil temperature [18] for which woven and nonwoven jute fabrics of lower fabric weight were experimented with and compared with plastic mulch and control (without mulch).

3.6 Soil Moisture

In a moisture barrier test (noncontact method) the woven and nonwoven samples behaved differently (Fig. 1). With the increase in fabric area density of nonwoven,

Fig. 9 Moisture evaporation through jute woven and nonwoven fabrics under the noncontact method



the thickness of the fabric increases and the fabric becomes more compact in structure. This improves control over the evaporation loss over fabric at lower area density. For woven samples, the number of openings increases with the increase in fabric area density without change in fabric thickness. At higher fabric area density, the study shows higher evaporation loss than lower fabric area density. The evaporation loss is higher in control followed by woven and nonwoven samples (Fig. 9).

In case of the contact method (Fig. 10) it has been found that the use of woven material to retain moisture in the soil has no significant effect compared to the control sample. The use of nonwoven samples restricts evaporation loss between 64 and 67 % compared to the control [16]. The structure of nonwoven samples with a higher area of coverage may be the reason for the restriction of moisture evaporation. However, there is no significant effect of fabric area density under study on evaporation loss. In field experiment, these lightweight jute nonwoven fabrics as mulching material attain significant improvement in yield of vegetables, horticulture fruit, and medicinal plants due to retention of soil moisture [30, 31].

3.7 Soil Temperature

The observations on temperature change are shown in Fig. 11. In the case of the effect of mulching on soil temperature, the initial soil temperature for all specified jute geotextiles, black polyethylene and control being the same, it increased or decreased with the change of ambient temperature in accordance with the morning or evening hours. However, the graph reveals that soil temperature in the pot with plastic mulch showed a higher temperature level among all the materials tested whereas the soil temperature in the pot with 250 g/m^2 nonwoven jute cover was much less as compared to control. The woven JGT of 200 g/m^2 was not able to

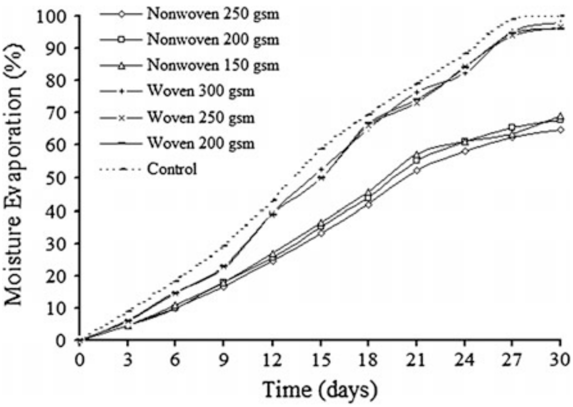


Fig. 10 Moisture evaporation through jute woven and nonwoven fabrics under the contact method

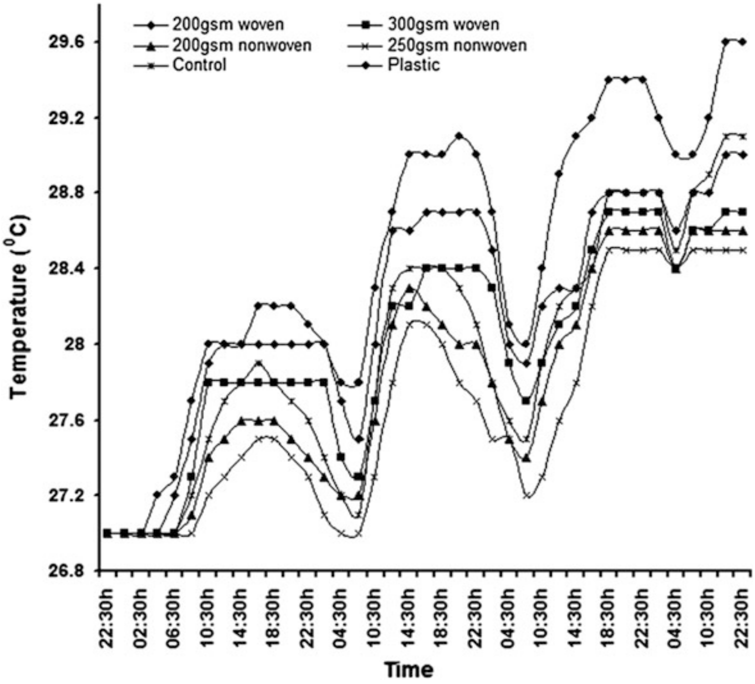


Fig. 11 Soil temperature profile with various mulching materials

influence much in controlling the soil temperature as the temperature profile was observed to hover around the control. The control of soil temperature was found to be most effective with 250 g/m^2 nonwoven followed by 200 g/m^2 nonwoven, 300 g/m^2 woven, 200 g/m^2 woven, control and conventional plastic material. This phenomenon is due to 250 being a thicker material with less pore space/void acting as an insulator neither to allow the inside heat to go out nor allow the outside air to pass through and heat the plants. As the thickness of the nonwoven material reduces, the porosity increases, which in turn reduces the insulation of nonwoven. The percentage of open area in the case of woven geotextiles is more as compared to nonwoven materials hence the insulation property also reduces proportionally. Black polyethylene sheet being the absorbent of solar heat increases the air temperature in the vicinity of plants and thus increases the soil temperature more than that of control. Soil temperature with time (beyond 3 days) shows an increase in trend due to reduction in soil moisture as depicted in Fig. 11. The soil moisture evaporates with time, which generates latent heat in the soil, and thereby the soil temperature reduces initially but with time the moisture evaporation reduces resulting in an increase in soil temperature.

4 Geo-Jute for River Bank Protection: A Case Study

The use of fibers for textile purposes is of mankind’s oldest art. Until about a hundred years ago, all fibers employed by man were from natural sources. The new millennium will see the emergence of a variety of eco-friendly new fibers with multifold end uses developed from natural fibers, synthetic fibers, and combinations of both of them. Natural geotextiles are predominant in the field of soil erosion through vegetation in the developed countries. Their present demand is about 86 million m^2 to which the contribution of jute is around 15 million m^2. Indian export of the material in 1996 was 2 million m^2 only, which appears to be very low being a country where half of the global output of jute is produced [21]. By the end of the century, the demand for natural geotextiles will be around 105 million m^2.

Geotextiles have been used effectively for erosion control and other civil engineering applications in the United States and Europe since around 1950. But in India, application of geotextiles is in the infant stage [26]. Natural geotextiles (e.g., geojute) has been experimented with in India as a bioengineering measure for slope stabilization and the prevention of riverbank erosion and the results were very encouraging.

India with 328 million hectares of land is posed with the problems of watershed management, soil and water conservation, and management of degraded and denuded habitats [34]. In the majority of cases jute/natural geotextile application may solve the problems. It has been observed by R&D organizations in India and abroad that the best cover is vegetation in the form of grass, bush, and legumes, as well as trees, which develop a binding force as high as 2.5 tonnes/m^2 of cohesion in the soil. This force is enough to arrest erosion. Unfortunately, the Indian community is very reluctant to adopt this technological advantage [27].

4.1 Soil Experimental Procedure

4.1.1 Materials

In the present investigation, jute geotextile woven fabrics of 305 gsm (heavy Hessian) and 645 gsm (B-Twill fabric) and nonwoven fabrics of 200, 250, and 300 gsm have been taken up for field trials on riverbank protection. Constructional details of the woven and nonwoven fabrics and their related physical and mechanical properties are given in Tables 5 and 6, respectively [4].

4.1.2 Methods

A suitable plot or site stretching about 50 m long on the Ganges riverbank in Guptipara village of the Hooghly district of West Bengal was selected which is prone to erosion due to rise of the water level in the river and velocity of an eddy current near the bank [23]. The relevant soil properties of the experimental zone are given in Table 7.

The bank was first cut to a suitable slope of 30°, approximately the same as the angle of internal friction of the bank soil. The surface was leveled and made free from angular projections, undulations, soil slurry, and mud. JGT rolls were unrolled and placed along the slope from the top down to the lowest water level. Care was taken to see that JGT was laid with the overlapping in the direction of water flow. More rolls were rolled along the length of the bank and two layers of the same area/fabric density were placed one upon the other with sufficient overlap (Fig. 12) [23]. JGT was fixed to the bank with the help of bamboo pegs in either direction. Care was taken to ensure that JGT did not suffer damage due to puncture, tear, and similar operational stresses and it touched the bank slope at all points (proper drapability). Suitable grass seeds were then spread on the treated bank for better stabilization. The schematic diagram of the experimental set-up is presented in Fig. 13. The growth of grass was observed at 15 days' interval by determining the average number of seedlings per unit area and the average length of grass; the observations are represented graphically in Figs. 14 and 15, respectively.

4.2 Results and Discussion

The experimental results on the growth of vegetation in terms of number of seedlings per unit area and average grass length are presented in Figs. 14 and 15. It is evident from these figures as well as from visual observations (Fig. 16) that the nonwoven fabrics showed a higher growth rate of seedlings (i.e., both coverage and growth) as compared to woven fabrics. Expectedly, the control sample (i.e.,

Table 5 Physical properties of nonwoven and woven jute geotextile fabrics

Parameters	Nonwoven			Woven	
Fabric weight/area density (g/m^2)	200	250	300	300	645
Thickness (mm) under 2 kPa pressure	1.30	1.56	2.05	1.25	2.50
Ends/dm	–	–	–	55	51.08
Picks/dm	–	–	–	47	31.50
Cover factor	–	–	–	14.8	20.7
Warp (tex)	–	–	–	265	387
Weft (tex)	–	–	–	261	752
Water absorption capacity (%)	275	225	156	414	684
Pore Size	60	49	41	160	110
Water permeability l/m^2/s at 10 cm water head	30	36	38	60	45

Table 6 Mechanical properties of nonwoven and woven jute geotextile fabrics

Parameters		Nonwoven			Woven	
Fabric weight/area density (g/m^2)		200	250	300	300	645
Tensile strength		0.61	0.69	0.98	1.99	3.05
Flexural rigidity (N/cm)	machine/warp	9.32	11.60	12.33	45.71	80.78
	cross/weft	22.34	24.16	43.54	34.53	65.32
Bending modulus (N/sq m)	machine/warp	56.04	50.28	27.14	842.73	691.81
	cross/weft	134.36	104.77	95.85	364.67	532.80
Puncture resistance (Kgf/cm^2)		40	62	68	78	143.00
Water retention (%) after 180 min		425.42	512.55	652.30	102.25	196.30
Moisture evaporation loss (%) after 3 days		68.5	65.43	62.84	97.95	105.60
Extension (%)		17.0	19.5	21.4	9.1	15.80

Table 7 Properties of Soil of the experimental zone (Guptipara) district Hooghly,West Bengal

Natural moisture content (% Wet Basis)	36
Bulk density (kg/m^3)	1,800
Plasticity index	22.0
Clay fraction (%)	38
Apparent cohesion intercept (kPa)	350
Effective angle of internal friction	30–32°

the bare surface) yielded the lowest growth parameters and ultimately led to the formation of wide gullies (Fig. 17). However, among the nonwoven fabrics, 300 g/m^2 exhibited the best performance followed by 250 and 200 g/m^2 and among the woven fabrics, 645 gsm (sacking fabric) furnished slightly better performance over 300 g/m^2 (heavy Hessian).

Jute geotextile generally retains moisture up to 11–15 % and when it is laid in contact with the soil surface, it helps in moisture conservation around 15–36 %, which sustains even during water stress conditions. Moisture plays the key role for

Fig. 12 Laying of jute nonwoven fabric rolls on the river bank

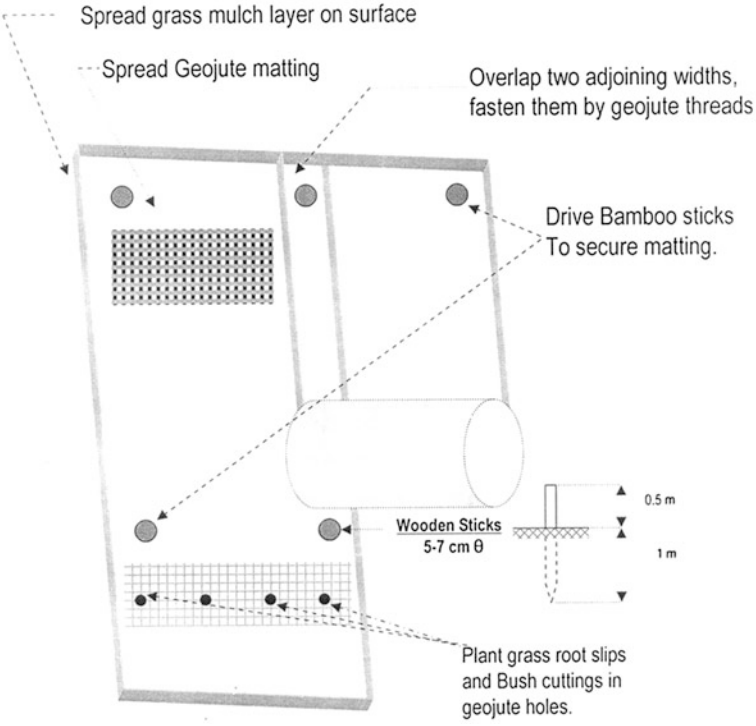


Fig. 13 Schematic diagram of experimental set-up

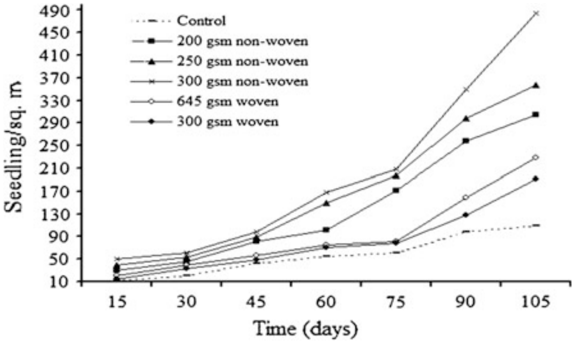


Fig. 14 Extent of vegetation with different fabrics

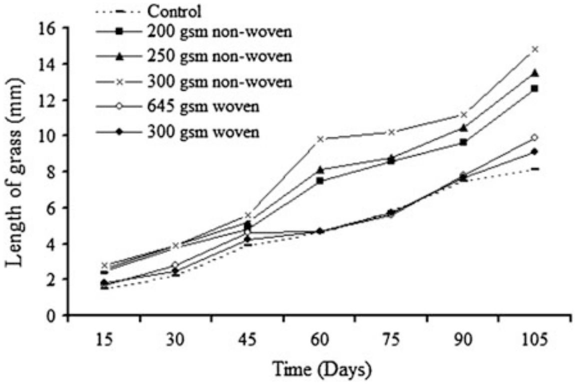


Fig. 15 Grass length with different fabrics

Fig. 16 Growth of vegetation on the river bank

Fig. 17 Formation of a wide gully on the bare riverbank

growth of vegetation as germination starts after just 7 days and moisture in the deeper layers can sustain tender plants. It is apparent that there was still some moisture even after 3 months from the date of the laying of jute geotextile to help plant growth. The contrasting feature was insignificant growth of vegetation in the bare/unprotected soil even at the end of 3 months because of constant evaporation of moisture from the top surface and thereby subjecting the topsoil to erosion. Geojute being biodegradable provides the microclimate necessary for initial vegetation as well as mechanical support to the plants to sustain themselves on a sloped surface (30–40°). The seedlings mature during the process of biodegradation of the fabric with the increased availability of N, P, K and other minerals in the soil, in other words, jute materials being transferred from the fabric to the soil. However, the rate of degradation of jute nonwoven is faster than woven fabrics such as sacking and heavy Hessian, which actually leads to faster growth of seedlings in the vertical direction and coverage in the horizontal direction. Moreover, water retention percentages being highest in the case of 300 g/m^2 nonwoven (as per Table 6), growth parameters are also equally highest for 300 g/m^2 and therate of growth decreases in order of decreasing water retention percentage of other nonwoven and woven fabrics. The growth of grass root reinforcement of the soil in the geotextile treated area was faster and sustainability of the riverbank took place [23].

5 Efficient Management of Soil Moisture by Jute Agrotextile for Cultivation of Horticulture Crops in Red Lateritic Zone: A Case Study

The economic value of most horticultural crops justifies the modification of the crop's microenvironment to accelerate growth, improve quality, and/or extend the growing season. Mulches are very useful for maintaining uniform moisture conditions in the orchard. Water loss through evaporation is decreased, and soil erosion is decreased as the impact of a heavy rainfall is reduced by the layer of mulch. The beneficial effect of mulches includes better control of weeds. Herbicide savings with mulches were found to range from 75 to 100 % and soil moisture levels are usually higher under mulched than unmulched soils because mulch acts as a vapor barrier, which reduces evaporation [25]. Organic mulch materials including paddy straw, sugarcane trash, rice husk, leaf litter and grasses, and inorganic synthetic materials such as polyethylene sheet are used in the case of horticultural crops. But the use of organic mulches might sometimes create problems such as reduction in infiltration rate, retention of high moisture content, and poor soil aeration. Studies showed that organic mulches such as paddy straw and water hyacinth were not very effective in controlling weeds, but black polyethylene proved most efficient suppressing weed growth to a great extent [37]. However, the conventional black polyethylene mulch films are costly, inconvenient due to rise in soil temperature [20], and are not biodegradable which causes problems for their disposal. Therefore, interest in the development of biodegradable mulch films with short service lifetimes has grown [38]. When undecomposed organic mulches are applied, there may be build-up of termites in the soil, which will damage the crop. Removal and disposal of conventional mulch films are costly and inconvenient. Moreover, they are not biodegradable which causes problems for their disposal. Plastics will not biodegrade in anyone’s lifetime. Hence, in view of the limitations of traditional mulches, efforts are being made for developing biodegradable mulches with short service lifetimes.

Hydramulch is a biodegradable mulch material comprising cotton by-products, newspaper, gypsum, and a proprietary adhesive. Muskmelon and bell pepper shoot growth were significantly lower with hydramulch compared to polyethylene mulch. Marketable yields of muskmelon and pepper with hydramulch were only 56 % and 7 %, respectively, of the yield obtained with polyethylene mulch [39]. The yield increase over bare soil (control) varies depending on the crop and the mulch. In the case of tomato, chili, and watermelon, the highest number of fruits per plant or vine was recorded on black polyethylene. The increase (average of 2 years) was 64 % in tomato, 36.6 % in chili and 47.9 % in watermelon over control [9].

5.1 Materials and Methods

From February to March, the sweet lime orchard and from October to November, the vegetable garden require high moisture in the soil, but due to dry belt, it is not possible to give flood irrigation. But plants produce profuse flowers if the moisture content in the soil is very high. In this connection, jute agrotextile may retain moisture in the soil if drip irrigation or less water is provided, which helps to give a better yield. Field experiments on soil moisture conservation by using jute mulch for cultivation of cauliflower, tomato, beans, and sweet lime were undertaken in a demonstration farm of Seva Bharati Krishi Vigyan Kendra at Kapgari village, Paschim Midnapur, West Bengal, India [33].

5.1.1 Climate

The experimental plots were located in a subtropical area at 22° 16′ latitude and 87° 22′ longitude with an average annual rainfall of 120–140 cm, 90 % of which is received from June to September in the rainy season. The temperature during the winter falls to 16–17 °C and rises up to 40–42 °C in the summer. Evapo-transpiration rates are usually high, and may be up to 2,400 mm per year resulting in an increased need for water. Except during the rainy season, the relative humidity is very low.

5.1.2 Soil

The soil is loam–clay loam with higher organic soil, pH 6.5–7.0 in the drought-prone red and lateritic zone. The soil is poor in water holding capacity but high in water absorbing capacity. The soil is rich in iron, but lacks Ca, Mg, S, Zn, Mo, and so on, and organic matter. Texturally, it is sandy loam soil.

5.1.3 Experimental Procedure

The experiments on vegetable cultivation were laid out in randomised block design (RBD) with three vegetables—cauliflower, tomato, and beans—and four types of jute nonwoven agrotextile mulch of fabric densities 150, 200, 250, and 300 g/m^2 excluding control as shown in Table 8. The farm inputs were provided as mentioned in Table 2 and other cultural practices such as plowing, manuring, plant protection, intercultural, and the like were adopted as per normal procedure. Before laying the geotextiles, the soil was fine-tilled manually followed by application of fertilizers in required doses. After laying of mulch covers, holes were pierced in the fabric to plant the seedlings through these holes. Subsequently irrigation was provided as per schedule. The crops were harvested according to their individual harvesting schedule (Table 9) and weighed plotwise after cleaning to get their respective yields. Each experiment was replicated five times and the average yield of each crop has been recorded as shown in Fig. 1. Tests of significance on the effect of specified fabrics on yield were conducted by regression analysis [29].

The experiments on sweet lime were undertaken in a 10-year-old sweet lime (*citrus sinensis)* orchard of 1.2 hectare area with planting density of about 300 plants/ha. The plant spacing between row-to-row and plant-to-plant was 6 × 6 m^2. The canopy area of each plant is approximately 18.30 m^2. Jute nonwoven fabrics

Table 8 Experimental design

Cauliflower 150 g/m^2	Cauliflower 200 g/m^2	Cauliflower 250 g/m^2	Cauliflower 300 g/m^2	Cauliflower Control
Tomato 150 g/m^2	Tomato 200 g/m^2	Tomato 250 g/m^2	Tomato 300 g/m^2	Tomato Control
Beans 150 g/m^2	Beans 200 g/m^2	Beans 250 g/m^2	Beans 300 g/m^2	Beans Control

Plot size 17.4 × 10.8 m^2 ; *Bed size* 3 × 3 m^2 ; *Gap between beds* 0.6 m

Table 9 Details of farm inputs provided

Crop (variety)	Harvest time (days)	Organic manure (kg/m^2)	Urea (kg/ m^2)	Muriate of potash (kg/ m^2)	Super phosphate (kg/m^2)	No. of irrigation	Weeding
Cauliflower (white contessa)	55	2	55	35	35	6	Nil
Tomato (JKTH-1195)	74	2	60	35	35	5	Nil
Bean (S–9)	34	1.5	40	20	20	4	Nil

of 150, 200, 250, and 300 g/m^2 excluding control were taken for determination of effect of jute mulch cover in sweet lime yield. Before application of mulch, the field was deweeded manually and the soil was prepared as fine tilth, and plowed 2–3 times by power tiller operation. During the final plowing, cow dung manure, di-ammonium phosphate, single super phosphate, and muriate of potash were mixed with the soil. A jute felt piece 2 × 2 m^2 was cut into four pieces and placed uniformly around each plant/tree of the orchard so that there was no uncovered top surface centering around a plant. After spreading of jute felt, it was wet by water and at a fortnight interval, spraying of Dursham @3 ml/l of water was continued for a period of 1 month for termite control. This experiment was replicated five times in different locations in the same orchard with each of the four types of jute agrotextile. The average yields of sweet lime have been recorded and presented in Fig. 2 [9]. These show that the application of jute nonwoven agrotextile mulch is very suitable for cultivation of different vegetable crops with higher yield and ensures sustainable growth in agriculture as the process is environmentally friendly.

5.2 Results and Discussion

It is evident from Fig. 18 that the yield of cauliflower has increased 1.5 times over control with 250 g/m^2 fabric. This was due to higher moisture absorption by the thicker material and subsequent availability of more moisture at the root zone as compared to lower thickness materials. However, thicker material of 300 g/m^2 due

Fig. 18 Yield of vegetables by jute mulch of different fabric area densities

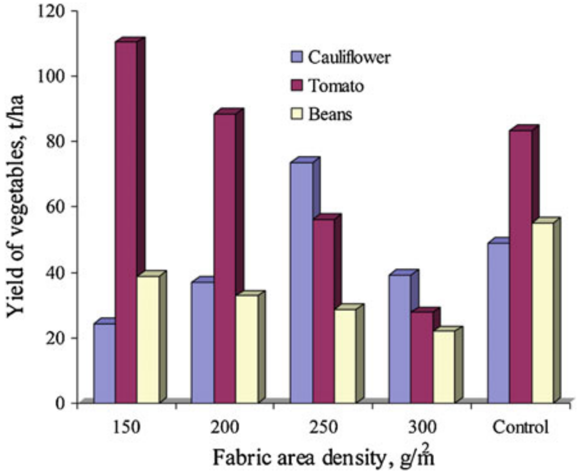
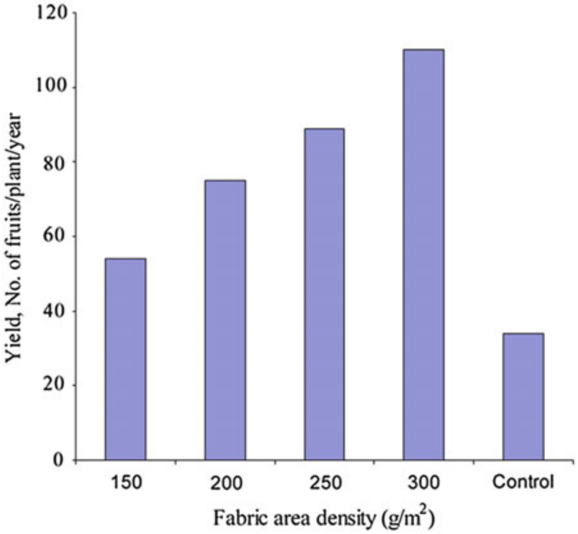


Fig. 19 Sweet lime yield by jute mulch of different fabric densities



to its more compactness retarded smooth moisture migration [38] and created flooding at the root zone showing lower yield. It is evident from the observations that tomato yield was maximum, about 110 t/ha under 150 g/m^2 fabric and it decreased with increase in fabric density. Higher-density fabric due to its greater thickness retains more moisture [16] and delivers excess moisture at the root zone which is not conducive for proper plant growth, which has been manifested in the form of yield. Predictably, the control plot has furnished more yield as compared to yields obtained with 250 and 300 g/m^2 fabrics which caused flooding at the root zone. Contrasting observations have been obtained in the case of beans where, the control plot, that is, the plot without any mulch cover, has yielded the maximum, 55.1 t/ha. This phenomenon does not underline any requirement of mulch cover for augmenting yield. Excess moisture in addition to its requirement reduces the prospects of getting a good yield [31].

The normal yield of sweet lime at Nagpur and Pune, Maharashtra, India, the traditional areas of cultivation, is 200–250 fruits/plant/year. Due to different constraints in the experimental area, the normal production was found to be 30–40 fruits/plant/year. From Fig. 19, it is evident that with the increase of fabric weight, the yield of fruits increased and it was maximum with 300 g/m^2 jute felt [6]. This increase in yield was due to the increased water holding capacity of the jute felt which is required to tide over the water-stress crisis condition occurring during flowering season of sweet lime plants which helps towards ensured pollination and higher yield and found significant at 1 % or less [31].

6 Conclusions

From these studies the following conclusions can be drawn:

Woven jute agrotextiles perform better in geotechnical applications where strength parameters such as tenacity, initial modulus, and secant modulus are predominantly required, such as in reinforcement functions including riverbank protection, cut-slope protection, road construction, and so on, for sustainable development. Nonwoven jute fabrics show lower permeability and higher water retention characteristics than their woven counterparts find favor in applications where separation and drainage functions are involved. Its higher moisture-holding capacity coupled with biodegradability makes it eminently suitable for applications such as mulching, erosion control, etc.

As far as soil moisture and temperature are concerned, the results and discussions show that yarn fabric weight and type of lightweight jute fabric have effects on controlling jute nonwoven of 250 g/m^2 giving the best effect; that is, the soil temperature was around 0.5 and 1.6 °C lower than the control (without any mulch) and plastic mulch, respectively. Jute nonwoven of 250 g/m^2 also prevents higher moisture evaporation loss compared to other woven and nonwoven fabrics.

Jute nonwoven of 250 g/m^2 fabric may be considered as better mulch over plastic mulch material to get extra yield in the cultivation of vegetables and fruits in arid regions. Nonwoven fabrics due to their higher water retention characteristics than their woven counterparts and coupled with biodegradability are best suitable for erosion control and perform better in geotechnical applications such as riverbank protection.

Mulching with jute geotextiles increased the yield of cauliflower substantially around 50 % and that of tomato to a lesser extent around 32 %. It had a practically insignificant effect in the yield of beans. A maximum yield of 73.66 t/ha of cauliflower was obtained with jute nonwoven fabric of 250 g/m^2 (control 49.08 t/ha) whereas tomato's increased yield was 110.39 t/ha with 150 g/m^2 fabric as compared to 83.39 t/ha achieved under controlled conditions. However, beans had negative effect with mulching by nonwoven jute. Mulching with nonwoven jute (felt) of 300 g/m^2 fabric density increased the yield of sweet lime fruits substantially: more than 100 fruits per plant per year as compared to only 34 fruits per plant per year obtained under the traditional cultivation method. These ensure eco-friendly processes and sustainable soil health.

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