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Dhorali Gnanasekaran *Editor*

Green Biopolymers and their Nanocomposites

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Green Biopolymers and their Nanocomposites

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Preface

Polymer/plastic has been an inherent part of our daily life. Right from the ordinary polythene bags to encasing of a tech gadget, polymers have been used almost everywhere. Such type of polymers/plastic makes up a huge proportion of all the polymers/plastic waste in the world, particularly in the ocean. As useful as it is, polymer is not the most environmentally friendly material. Our constant use of it has seen huge amounts of it lodged in Arctic sea ice, penetrating into the deepest parts of the ocean and even traveling up the food chain. A recent survey shows that India is the third largest polymer consumer in the world, with a total consumption

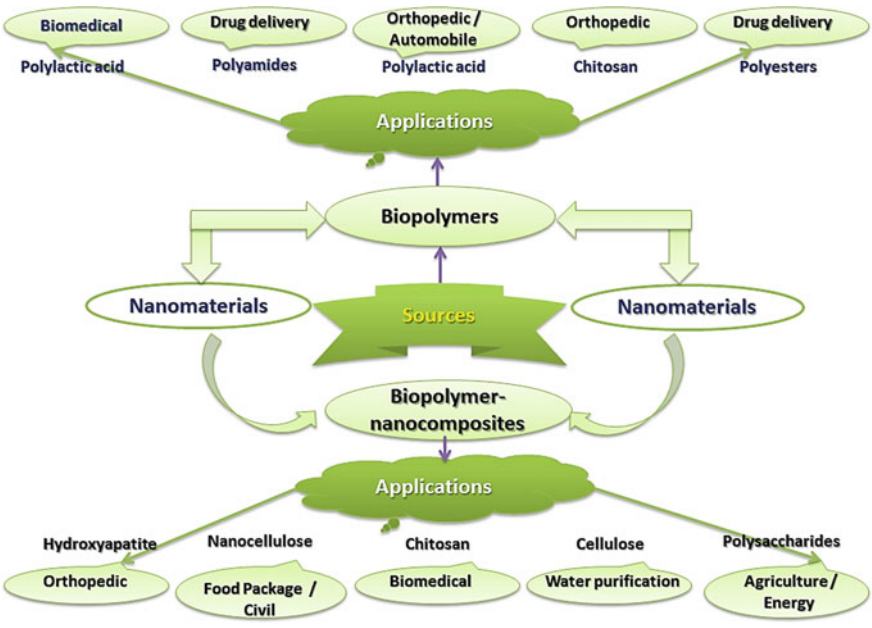

Fig. 1 Technical schematic representation of the theme of the book

of polymers of about four million tons and a resulting waste production of about two million tons.

Hence, there is an urgent need for the development of biodegradable polymeric materials that would not involve the use of the toxic or noxious component in their manufacture and could be degraded in natural environmental conditions. For these reasons, throughout the world today, the development of biodegradable polymeric materials, i.e., natural polymers with controlled properties, has been a subject of great challenge to materials scientists and engineers. New environmental policies, societal concerns, and growing environmental awareness have triggered the search for new products and processing that are benign to the environment. Hence, this book is proposed to focus on recent advances in biodegradable green polymers and their nanocomposites for several applications. The pictorial representation of the theme of the book is shown in the above (Fig. 1).

This book has been divided into 18 different chapters pertaining to the theme. The gist of each chapter has been explained briefly as follows:

Chapter 1 Scrutinizes the state of the art of biopolymer development from renewable resources for a variety of applications; provides awareness new environmental policies, societal concerns, and growing environment which has triggered the search for new products; and covers global biodegradable polymer market as well as its research scenario. Also, it covers plastic waste generation status, recent developments, and trends in green biopolymers.
Chapter 2 Discusses the current research efforts of PLA/fiber composites; the different preparation methods; and applications in automotive, construction, and packaging.
Chapter 3 Comprises challenges faced in direct blending PLA with other polymers and use of compatibilizers and/or plasticizers to improve processability and/or performance of resulting blends. It concludes with the future trends and recommendations that should enable the production of high-end performance PLA-based bioblends.
Chapter 4 Aims to provide an overview of the recent developments in nanocellulose-reinforced composites for packaging applications. It provides a solution to overcome problems mainly faced by the food industry.
Chapter 5 Gives an overview of the chitosan biopolymers, their properties, and their capability to be used in the food packaging industry.
Chapter 6 Looks into food packaging materials made from biopolymers (polysaccharides, proteins, aliphatic polyesters). Their types, sources, advantages, limitations, and future innovations are discussed.
Chapter 7 Discusses sources, types, and applications of nanostructured green biopolymers. Much emphasis is laid on their orthopedic applications in a quest to address the ongoing debate on "Whether most feasible areas to apply green biopolymers is in biomedicine or not?"

Chapter 8 Discusses the properties, structure, synthesis, and application of polysaccharides, polyesters, and polyamides in drug delivery. The ability to produce natural biopolymers with personalized properties *via* biotechnological techniques opens them up to several medical applications.
Chapter 9 Deals with different classes of PLA-based nanocomposites, their structure–property relationships, and a wide range of potential applications in various fields such as biomedical, food packaging, automobiles, agriculture, and renewable sources.
Chapter 10 Describes the biopolymers and their nanocomposites that have made tremendous progress in biofunctionality, biocompatibility, and biodegradability. It discusses the biomedical technologies such as tissue engineering, regenerative medicine, gene therapy, controlled drug delivery, and bionanotechnology.
Chapter 11 Looks at polymeric drug delivery systems, their morphology, nanomaterials, and particulates used for treatment, some plant extracts, mechanisms of drug delivery and risks associated with their usage, and their applications.
Chapter 12 Reviews the current research and development of the synthesis of biopolymeric for medicine and surgery. The efforts are geared toward the improvement of methodologies and devices for more efficient and effective processing, and the application of biopolymers in medicine and surgery is also explained.
Chapter 13 Focuses mainly on various techniques for green biosynthesis of composites and nanocomposites, specifically for applications in (bio)medical fields.
Chapter 14 Briefly explains types, areas of application, properties, and reasons for the selection of biopolymers in energy application and presents the future trend of energy applications.
Chapter 15 Examines in-depth applications of biopolymers and their nanocomposites in civil engineering infrastructures in order to meet the twin targets of sustainability and environmental friendliness which are vital to continued life on earth.
Chapter 16 Summarizes the current knowledge on polysaccharides, nanocomposite preparation using various methods, different types of nanocomposites, and properties of nanocomposites based on the structure and their applications.
Chapter 17 Presents a brief introduction of degradable polymers followed by an extensive review of versatile applications, i.e., agriculture, personal care, encapsulation materials, tissue engineering, regenerative medicine, and shape-memory materials.
Chapter 18 Provides a broader perspective of magnetic cellulose green nanocomposites and their use as an adsorbent for the removal of heavy metals from wastewater.

This book offers an excellent source for researchers, graduates, environmental and sustainability managers, business development and innovation professionals, chemical engineers, polymers manufacturers, agriculture specialists, biochemists, and suppliers to industry to debate sustainable and economic solutions for biopolymer nanocomposites. Most of the published relevant books discuss the

preparation, properties, and applications of biopolymers, which are prepared from a specific type of biopolymer and very specific nanocomposites. Therefore, it is planned to focus on the findings from the past two decades to recent advances in the preparation, properties, and applications of biopolymer nanocomposites, which are fabricated from different types of biopolymers with diverse nanomaterials (organic, inorganic, and organic/inorganic).

Although the structural characterization, physical and mechanical properties, processing, and commercial applications of various types of biodegradable polymer nanocomposite materials have been widely published in peer-reviewed journals, patents, conference proceedings, and edited books, to the best of the editor's knowledge, there is no single book that consolidates knowledge in these areas in a concise form. A single book of this nature will serve as a useful reference for students, researchers, engineers, and other professionals who are interested in this field. This book will also help industrial researchers and R&D managers who want to bring advanced green biopolymer-based products into the market.

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Chapter 1
Green Biopolymers and Its Nanocomposites in Various Applications: State of the Art

Dhorali Gnanasekaran

1 Introduction

Go green, Go natural! Green and natural are not the same, when it comes to polymers. The term "Green Polymers" appeared since 1990s, and generally, they are manufactured by using sustainable (or green) chemistry. The green polymer narrates the design and processes of polymer products that diminish or eliminate the use or generation of materials harmful to human, animals, plants, and the environment. The another type of polymer, for example, natural polymers (or biopolymers) that are found in nature and are polymers that occur naturally in plants and animals sources are produced by living organisms. Starch, cellulose, proteins, or lignin have structural function of the plant or animal (Fig. 1). Natural polymers are usually green; i.e., it won't be harmful. Hence, the green chemistry or green polymer pursues to diminish and avoid the pollution at its source. Therefore, the polymer industries are seeking substitutions to petrochemical bases to guarantee a sustainable long-term upcoming. Green biopolymers are an important part of research and development that continues to develop in its influence over industrial research. These are improvements which are focused by environmental concerns and interest in sustainability, the desire to develop "green" products that to reduce our dependence on petroleum and commercial prospects. The environmentally friendly (eco-friendly) polymers are not an entirely fresh (new or novel) material [1]. However, nowadays, due to the deal with enlarging global warming, CO_2 emissions, and finite natural fossil-fuel-based resources, the development of eco-friendly polymer has become considerable research interests, which have the correct balance of properties for a variety of applications.

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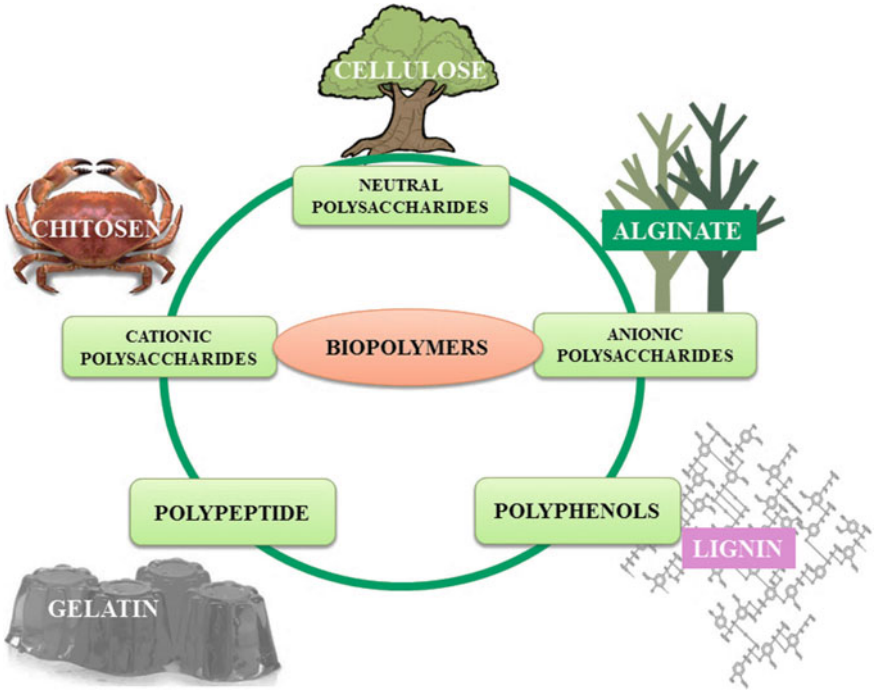

Fig. 1 Pictorial representation of origin of few biopolymers

The hawksbill sea turtle has been fighting free from polythene bags. The ocean of polythene garbage suspended in water over a Caribbean environment or sperm whale washed on to the land in Spain, its stomach occupied by plastic wastes. In the meantime the establishment of polythene in twentieth century, people has generated approximately 8300 million tons of the junk. About 3/4 have been wasted, and 80% of that has thrown into the environment. The 8 million tons of plastics a year end up in the ocean 5 trillion pieces and counting (Fig. 2). Due to this, the constant healthiness for all of us remains ambiguous, as consumed plastic works its way up the food chain. From forbidding plastic to restarting recycling systems to harnessing plastic-chewing bacteria, there won't be any shortage of touted solutions. It is not perfect what would work best [2].

Based on these circumstances, there is a vital requirement for the improvement of biodegradable polymeric that will not include the use of toxic or noxious materials in their manufacture and could be degraded in the natural environmental conditions. For these motives, throughout the universe today, the improvement of biodegradable things, i.e., natural polymers with controlled properties, has been a matter of great research task to the community of scientists and engineers. The pictorial representation of the life cycle of the biodegradable polymer has been represented in Fig. 3. Although natural polymers are less than 1% of the 300 million tons of polymers

Fig. 2 Photograph of ocean contaminated by polymer/plastics [44]

formed per year, their production is progressively rising. The market is driven by a growing demand for natural polymers with pharmaceutical, medical, and other applications [3]. Natural polymers are also used in construction, adhesives, food packaging, beverage industries, cosmetics, toiletries, biomedical, orthopedic, drug delivery, energy applications, civil engineering applications, water filtration, and agriculture in addition to paint and ink industries [4].

The global economic activities have been increasing a lot since past few years. This immense growth has been raised severe harms about present designs of manufacture and ingestion. As the modern community has developed its awareness in the empathetic of the environmental features and its industrial exercise, better consideration has been provided to the perception of maintainable economic structures that rely on energy from undepletable source and materials. Make uses of biologically derived/biodegradable polymers begin to be significant constituent of this global.

The following green principles include while manufacture of biopolymers [1, 3, 4]:

- The production process should be clean (no-waste);
- While manufacturing it needs high energy efficiency;
- No use of supplementary (organic solvents) substances;
- A high percentage of the raw material in product;
- High safety standards;
- Usage of renewable resources/energy;
- Low carbon footprint;
- The lack of health/environmental hazards;
- Well-ordered product life cycles with effective waste recycling (Fig. 3).

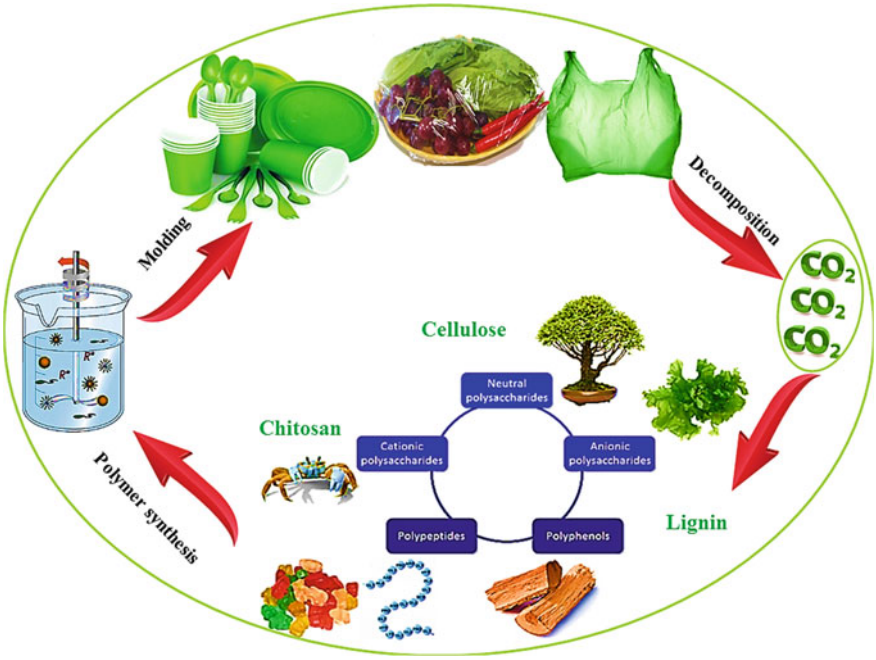

Fig. 3 Life cycle of biodegradable natural polymer

Furthermore, the usage of renewable assets for green polymer manufacture would not compete with food production, must not encourage deforestation, and must not custom transgenic plants or genetically modified bacteria; biodegradable plastics must not create inhalable pollen or nanoparticles.

The two significant benefits that biopolymers bring out are:

1. They do not carry any toxins that synthetic polymers carry; it (no toxins) is applicable to almost all biopolymers.
2. Some of the biopolymers are biodegradable—they quickly (within 2 months) disintegrate into CO_2, water, and starch, whereas synthetic polymers could take 100+ years (sometimes, even 500+ years) to disintegrate. It is not applicable to all biopolymers—that is, some biopolymers are not biodegradable. It is quickly clear that biodegradable polymers represent the most significant benefits and hence could make a significant difference to environmental sustainability. The expected imagination of eco-friendly of polymer with a human is shown in Fig. 4.

While most of the initial market opportunities for biopolymers will start in the developed countries, opportunities will be present in India as well. These chances are existing in a range of industries that include packaging, water, beverages, insulation materials, biomedical, orthopedic, drug delivery, specialty materials and more [5]. Also, biopolymers could be processed in same way to petrochemical polymers such as injection molding, extrusion, and thermoforming. There is the way to develop its

Fig. 4 Biopolymers environmental friendly with human. *Source* Daily excelsior [45]

tensile strength, than could be done with biopolymer blended with their copolymers or other polymers.

Biopolymers will be categorized into
Degradability based:

- Biodegradable polymers (PLA, PHA, starch blends, etc.)
- Non-biodegradable (moderately bio-based) products (bio-based PET, PE, combinations of PLA with conventional polymers).

Degree of replacement based:

- **Drop-ins**—polymers are non-biodegradable, acquired from renewable raw resources which have undistinguishable methodical properties to their fossil equivalents. They are partly bio-based, partly non-biodegradable product such as PE, PET, or PP.
- **Non-Drop-ins**—materials which can or cannot be decomposable, but they don't have undistinguishable characteristics to their fossil equivalents, include PLA, PHA, Bio-PA, etc.

Type	Biodegradable	Non-Biodegradable
Drop-ins	None	Bio-PE, Bio-PP, Bio-PET
Non-Drop-ins	PHA, PLA, Cellulose-based, Starch	Bio-Polycarbonate Bio-based Polyamide

Note Bio-based polymers may or might not be recyclable polymers; biodegradable polymers might or could not be formed from renewable assets; in fact, it is a general misconception that bio-based polymers are automatically recyclable and vice versa

Biopolymers are polymers in which all carbon atoms are obtained from renewable feedstocks. The carbon atoms may or may not be recyclable. Bio-based polymers

Fig. 5 Variety of packing materials prepared from biopolymers [46]

have both renewable and fossil-fuel-based carbon atoms. The proportion of bio-based components and the environments, under which the bio-based goods may be biodegrade, if at all, vary widely. As per the American Society for Testing and Materials (ASTM), a bio-based material is: organic components in which carbon atoms are resulting from a renewable resource through biotic mechanism.

Yields on the market those are prepared from a range of natural feedstocks comprising corn, potatoes, rice, tapioca, palm fiber, wood cellulose, wheat fiber, and bags. The yields are available for variety of applications such as bottles, bags, cups, plates, cutlery, carpets, bedding, furnishings, film, textiles, and wrapping materials (Fig. 5). In USA, ratio of bio-based ingredients needed for product to be denoted to as bio-based is defined by the United States Department of Agriculture (USDA) on a product-by-product basis. Institute for Local Self-Reliance (ILSR) had suggested that USDA sets a least threshold of 50% bio-based products to be considered as a bio-based.

According to the Biodegradable Products Institute (BPI), biodegradable materials are "where under the right conditions the microbes in the environment could breakdown the material and use it as a food source" or "a biodegradable materials are completely mineralized by microorganisms." Recyclable polymers are not essentially bio-based. Biodegradable and bio-based polymers are not the similar. Few bio-based products could biodegrade in municipal or commercial composting facilities, home composting, and aquatic and roadside environments, others have capacity to biodegrade in very particular environments, and some of them never biodegrade. The BPI is the third-party certifier in North America for products that are compostable in commercial composting facilities. To have the BPI Compostable Logo (Fig. 6), products should meet as per ASTM Standards D6400 (for Compostable Polymers) or ASTM D6868 (for Compostable Packaging). To get certified products according to the BPI, a product should:

- Breakdown quickly in the course of composting process;
- Biodegrade rapidly in composting environments;
- Not diminish the worth or utility of broken down compost;

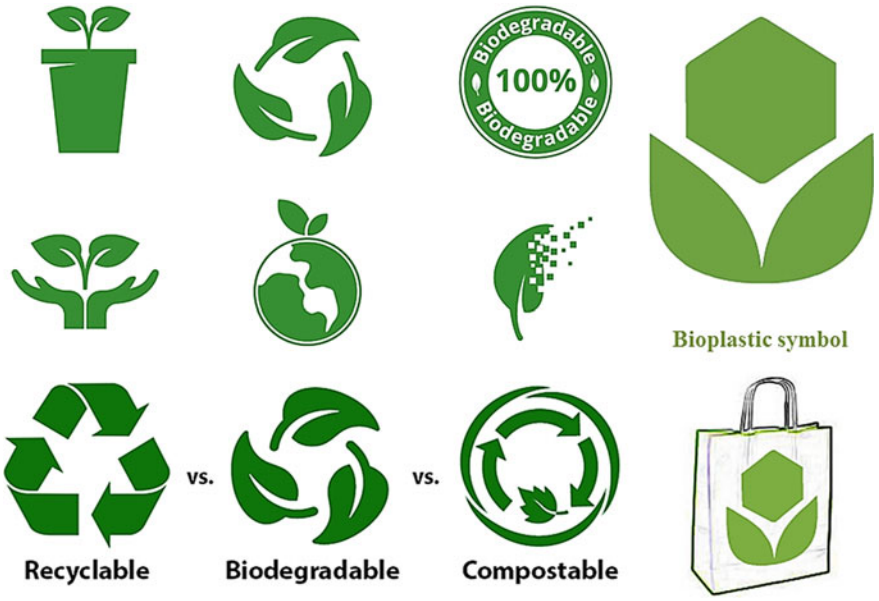

Fig. 6 Various types of notation of biodegradable symbols

Table 1 Comparison of biopolymer and conventional polymers

Advantages of biopolymers	Disadvantages of petro-polymer
It could replace various harmful conventional polymers	Non-renewable
It could be fully biodegradable	Health impacts
It could be prepared from a range of renewable assets	Non-biodegradable with devastating effects on the ocean life
It could be composted locally into a soil modification	Demand and production skyrocketing
It could pay to healthier rural economies	Polymers industry cares more drilling
Recycle and reuse	Recycling and reuse low

- The hummus prepared for the period of composting mechanism will care plant life;
- Doesn't have great volumes of regulated metals.

The available and most notational biodegradable symbols is shown in Fig. 6.

Biopolymers have numerous advantages over petro-polymers, but lots of tasks also lie ahead.

Potential benefits of biopolymers and problems with petro-polymers are shown in Table 1.

Challenges with improvement and well-known acceptance of biopolymers comprise:

- Concern on genetically revised organisms;
- Essential to improve composting programs and infrastructure;
- Lack of adequate labeling;
- The desire for sustainably mature biomass;
- Concern over pollution of recycling systems;
- The concern with nanocomposites and fossil-fuel–polymer blends.

2 Biopolymer Research Scenarios

Biodegradable materials from renewable resources have fascinated great responsive in modern years [3]. Renewable sources of polymers provide substitute to preserving sustainable improvement of economically and biologically smart technology. The modernisms in the improvement of polymers from biodegradable materials, the maintenance of fossil-based raw materials, complete biodegradable, the reduction in the volume of garbage and compostability in the natural sequence, protection of the weather through the reduction of CO_2 emission, as well as the application feasibilities of agriculture resources for the manufacture of green polymers are few of the justifications why such polymers have enticed the educational and industrial attentiveness [4]. So far, biodegradable polymers such as resources from renewable are used for the preparation of nanocomposites; they are polylactide (PLA) [6–12], poly(3-hydroxybutyrate) (PHB) [13] and its copolymers [14], thermopolymer starch [15–21], plant oils [1, 22–25], cellulose [26, 27], gelatine [28–30] etc.

In recent days, due to the new environmental policies, societal concerns and developing environmental responsiveness have triggered the search for novel products and processing that are benign to the environment. For the year 1990–2000, one of the quickly developing areas is the use of polymers for packaging. The polymer should have properties of convenience and safety, low price, and beautiful qualities are the significant factors defining prompt development in the use of polymers for fabrication of packing materials. In recent times, out of entire polymer manufacture, 41% is used in packing industries, and 47% of them are used for packing of only foodstuffs [3]. Those packing materials/polymers are commonly prepared from polyolefins (e.g., polypropylene (PP), polyethylene (PE)), polystyrene (PS), poly(vinyl chloride) (PVC), etc., and are mostly manufactured from fossil fuels, consumed, and thrown into the environment, windup as automatically non-degradable wastes. Therefore, amounting to 40% of packaging refuse is basically endless, and the polymer refuse is becoming a global environmental issue.

The majorities of decomposable polymers have an outstanding properties compared with many petroleum-based polymers, and they are rapidly biodegradable (Table 1) in nature, and also they are competing with commodity polymers. Therefore, biodegradable polymers have the maximum commercial potential for biopoly-

mers or bioplastics. On the other hand, few characteristics of the polymers, such as little heat distortion temperature, elevated gas permeability, brittleness, and low melt tackiness for further processing, limit their use in extensive range of uses. For that reason, fabrication of the decomposable polymers through advanced technology is a challenging mission for scientists. Nevertheless, nano-reinforcements of environmentally friendly polymers have displayed excessive potential in the design of eco-friendly polymers with the suitable characteristics. The novel kind of composite has launched, in which the reinforcing filler has nanometer (1–100 nm). Those are recognized as decomposable polymer nanocomposites [26].

By means of modern advancements in manufacture technologies and the finding of new well-designed monomers, research shows that biodegradable polymers with enhanced properties can be manufactured from renewable resources [22, 26]. Research articles and patents in these arenas are growing in academic, industrial, and government organization become involved in research and commercial activities. It gives an importance of green polymers, and Environmental Pollution Control committee scrutinizes the state-of-the-art improvements in generating conventional polymers from ecological sources.

3 Worldwide Biopolymers Market Scenario

As there is a need for suppression of usage of conventional polymers, there is a growth in the development of industries for biopolymers [12] manufacturing. Biopolymers are found to be wide recognition in various industries, on justification of its well-known eco-friendly characteristics. Nowadays, biopolymers are significant part of each sector of food technology, nanotechnology, agriculture, medical, chemistry, etc. Every year 20% increase in the fabrication of biopolymer products and bioplastics. The detail flow chart is given Fig. 7. The market of 1.2 million tons in 2012 could see a fivefold increase in production volumes by 2017, to almost 6 million tones. Probable, by 2020 biopolymers manufacture can rise to 12 million tones.

The term ‘biopolymers’ are employing for entire kind of products with dissimilar properties and uses. Biopolymers have been a source for many industries, such as advanced materials, transportation and automotive, banking and economic services, biotechnology, chemicals, consumer goods, power and energy, beverages and food, industrial automation, medical kit, pharmaceuticals, semiconductor and electronics, and telecommunications and information technology. In worldwide market, the implantable biopolymers and bioplastics were value nearly $156 billion in 2014. This market is predictable to develop at a yearly growth rate (CAGR) of 7.2% between 2014 and 2019 resulting in $155.7 billion in 2014 and $200.5 billion global market in 2019.

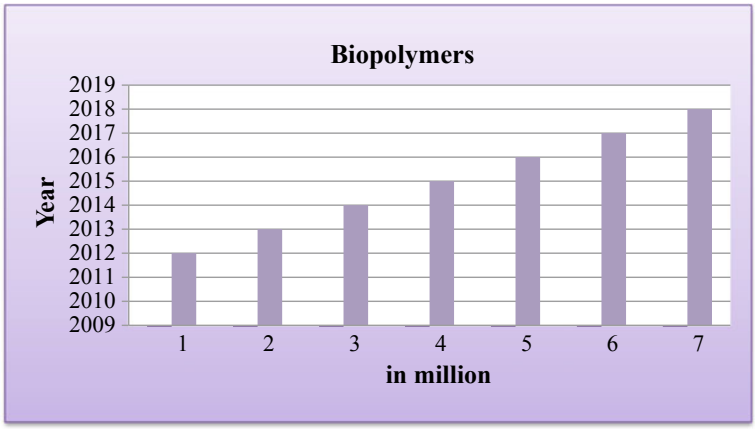

Fig. 7 Flow chart of biopolymer market—status

The market is determined by stringent environmental laws through the globe as biopolymers have a less harmful impact on the environment compared to conventional polymers. One more main feature which is estimated to bring momentum to this market is variations in the costs of oil compelling companies to look for a steady basis of raw material.

4 Global Production Capacity of the Biopolymer by Region-Wise and Market Segment-Wise

Nowadays, the consumption of petroleum-based polymer will be reduced by 15–20% by 2025 due to biopolymers and bioplastics are available for the last decade. Due to the improved biopolymer's properties and its innovations exposed the new market and applications with greater profit potentials in medicine, automotive and electronics. Currently, most of the manufactures are fabricating the biopolymers and bioplastics that are biodegradable and can be made from a wide ranging of plants. When biopolymers and bioplastics manufacture companies are changing their approach from replacing current products to fresh applications, product formations, and production methods, cost-effectiveness and scalability grown dramatically. In 2025, Europe will have 31% share, the USA will have 28% share, and Asia will be the most important market with a 32% share of the global total demand. Asia has the benefit that genetically altered plants are easier to realize and novel outlets for agriculture are quicker to build up. In 2017 and 2022, global biopolymer production by region-wise has shown in Fig. 8a.

The green polymer (biopolymer) business develops to 8–10% per year. The green polymer (biopolymer) cover around 10–15% of the total conventional polymers busi-

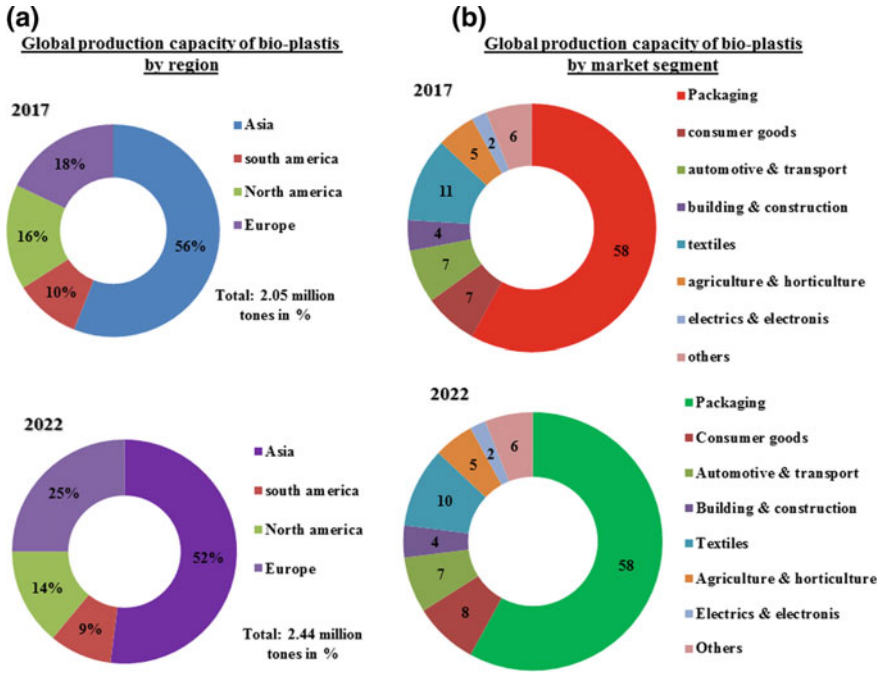

Fig. 8 **a** Global production of bioplastics by region and **b** Global production of bioplastics by market segment. *Source* European bioplastics [31]

ness and will increase market share to 25–30% by 2020. The biopolymer or bioplastic market itself is vast; it extended over US$1 billion in 2007 and is predictable to cross US$10 billion by 2020. The growing figures of companies are very descent into and financing in this segment. The new applications and revolutions in the automotive and electronic engineering industry lead to a market boom. More than 500 green polymer manufacturing companies are presently on stream, with the number expected to boom further 5000 by 2025. In 2017 and 2022, global biopolymer production by market-wise has shown in Fig. 8b.

Packaging is anticipated to the highest market share during the projected period. Green polymers and its nanocomposites are broadly used for food package, cosmetics, pharmaceuticals, and goods packaging. Most of the countries are prohibiting the conventional polymers' usage due to environmental contamination as these polymers finally end up in the sea or in landfills. The ratios of landfill, incinerated and recycled, have shown in Fig. 9. Governments are inspiring the use of biopolymers by giving subsidies and charging taxes on the use of conventional polymers.

The packaging market accounts for (and is set to retain) 58% of biopolymer production, and the details are shown in Fig. 8b. Meantime, European country is planned to increase their share of worldwide manufacture from 18 to 25% in coming 5 years (Fig. 8a). Since globe production is forecast to increase by 20% for same

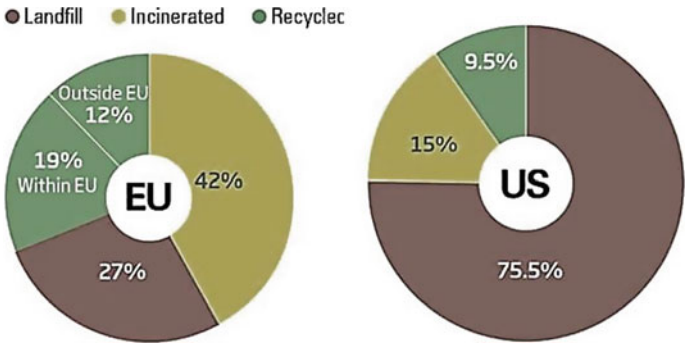

Fig. 9 Level of plastics waste on the EU and USA

period, this reflects a enormous increase in European capacity—a fact highlighted by the numerous manufacturers existing in Berlin who declared the ideas to launch or scale-up production [31].

Bio-based polymers are not only offering advantages on raw materials side however also on the disposal side via definite promising end-of-life (EOL) choices. Particularly waste discarding with energy regaining has an extra advantage, which falls in acquiring carbon neutral energy while permitting several uses for possible recycling. The Commission declared that all of the compost comprising biodegradable materials could be categorized by means of a risk assessment system at a higher toxic level. Biopolymer waste could be treated by aerobic degradation, composting, or anaerobic digestion. While biopolymers are digested, its discrete carbon and hydrogen content are recycled naturally. The biggest sector of the market, packaging, is predicted to reach nearly 1.7 billion pounds in 2016. In 2011, market was estimated to 656 million pounds, making the 5 year CAGR 20.5%. Another largest sector, i.e., fibers, is expected to grow 134 million pounds in 2011 to 435 million pounds in 2016, for a 5-year CAGR of 26.6%.

Nowadays, few companies are promising to reduce greenhouse gas emissions by 20% between 2015 and 2030 and to work toward 100% recyclable, compostable, or biodegradable packaging by 2025. The adoption of biopolymers is, therefore, an acknowledged key component of its long-term sustainable packaging strategy. Seven different types of plastic packaging have been given codes to aid domestic recycling, but in the UK, as elsewhere, very little is actually recycled are details are given in Fig. 10.

Few popular companies are introduced into a new type of water bottles, which are an uncommon inventiveness in that the world's famous bottle water enterprises are functioning together to generate a future generations' biodegradable PET water bottles. It is expected to succeed industrial scale PET resin production of 75% bio-based feedstocks by 2020, it may growing to 95% by 2022 (Fig. 11). The inventiveness is fully lifecycle assessment (LCA) audited and is scrupulously circumvent distracting

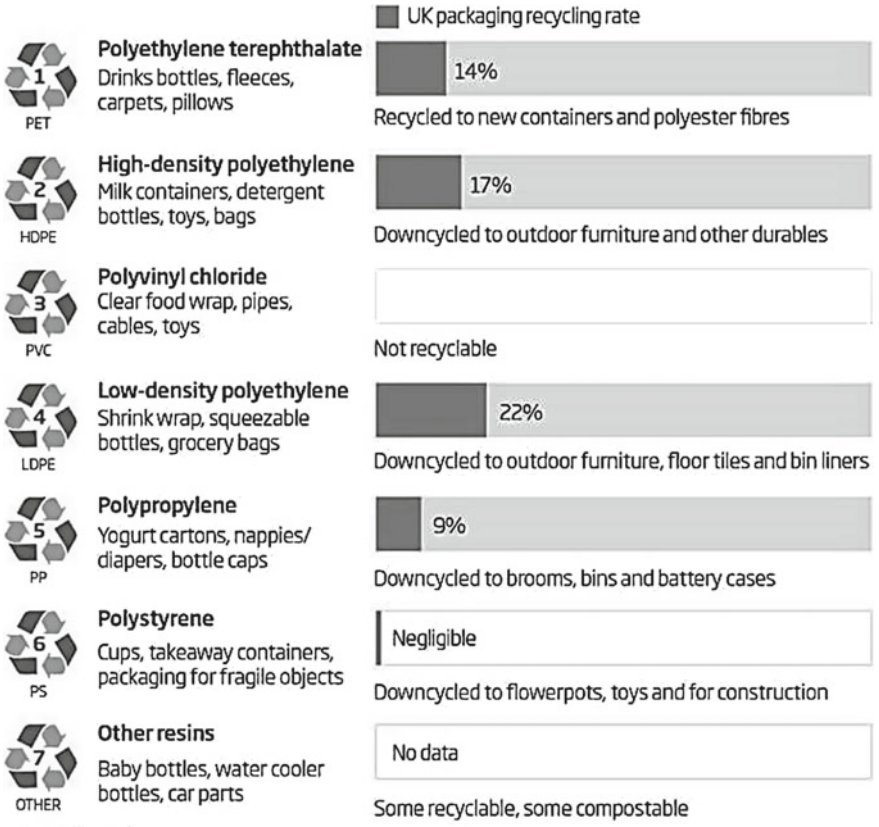

Fig. 10 Low recycling rates of different types of polymers. *Source* WRAP/RECOUP

resources from food production, planning to use the second-generation lignocellulosic biomass.

4.1 Expanding Possibilities

A bio-based polymer in the packaging trade needs to begin receiving enthusiastic about is polyethylene furanoate or PEF. PEF is a new, 100% bio-based polymer whose properties are very comparable to PET and ecological within the PET stream. The chemical structure of PET and PEF has shown in Fig. 12. However, apart from its renewable quality, PEF executes better than PET, contributing extraordinary shelf-life and downgauging chances in rigid and flexible uses. PEF as carbonated soft drink bottle that has demonstrated that 6 times better carbon dioxide barriers and 10 times better oxygen barriers.

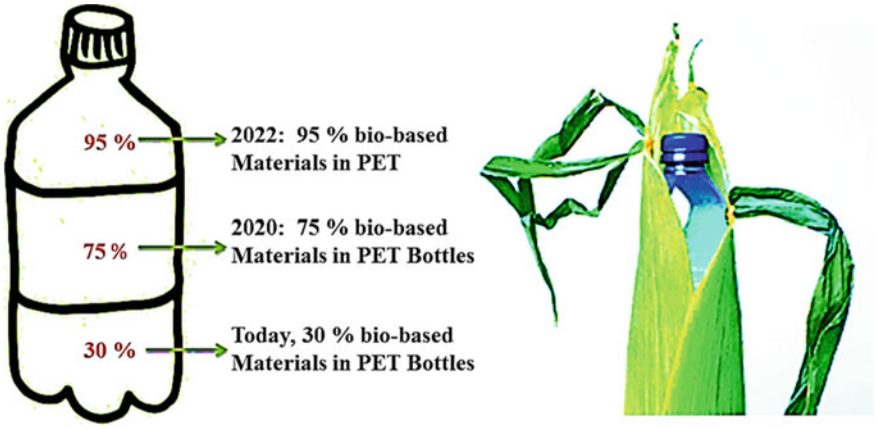

Fig. 11 Graphical representation of increase % of the use of bio-based PET bottles

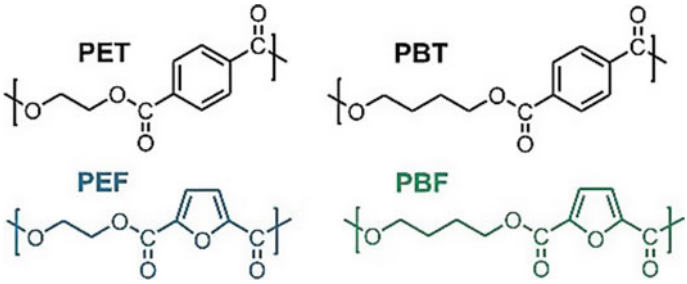

Fig. 12 Chemical structure of PET, PBT, PEF, and PBF

In the meantime, considerable discussion focused on the potential of biopolymers in packaging process—the best challenging material to our existing recycling process due to the range and complexity of substrates used. Biodegradable and flexible are a potential answer to this issue, with the additional benefit that they may exist an opportunity to divert food waste away from landfill. Similarly, developments such as biodegradable functional coatings and bio-based multi-layer barrier films may prove another significant pathway to sustainability.

Advanced bio-based polymers such as PLA (polylactic acid) and PHAs (polyhydroxyalkanoates) are the leading drivers of this development in the arena of biodegradable polymers. PHAs are significant polymer family which has been in improvement and now go into the market at profitable scale with fabrication capacities threefold in next 5 years. Polyesters are 100% bio-based, decomposable, recyclable, and biodegradable and feature a wide range of physical and mechanical characteristics depending on their chemical structure. Production abilities of PLA are also expected to develop by 50% by 2022 compared to 2017. PLA is versatile substance that features out-

standing barrier characteristics and it is obtainable in high-performance PLA ratings that are an ideal substitution for PS (polystyrene), PP (polypropylene), and ABS (acrylonitrile butadiene styrene) in further challenging applications.

Non-biodegradable polymers, bio-polymer, including drop-in solutions bio-based PE (polyethylene) and bio-based PET (polyethylene terephthalate), in addition to bio-based PA (polyamides), presently makeup for about 56% (1.2 million tons) of universal biopolymers manufacture capacities (Fig. 7). The production of bio-based PE is expected to continue to grow as new scopes are scheduled to publish online in Europe in upcoming years. The purposes to rise manufacture volumes for a bio-based PET, however, have not been perceived at the rate expected in preceding years. Alternatively, the attention has shifted to the improvement of PEF (polyethylene furanoate), a novel polymer that is projected to arrive in the market on 2020. PEF is equivalent to PET however 100% bio-based and is said to characteristic superior barrier and thermal properties, making it perfect material for the packaging of drinks, food and non-food products. Bio-based PP is predictable to enter the market in 2022 on a commercial scale with strong development prospective due to extensive application of PP in a variety of areas.

Packing process remains the major area of application for biopolymers with nearly 60% (1.2 million tons) of the total biopolymers market in 2018. The statistics also proves that biopolymers are already have been used in several other divisions, comprising textiles, consumer goods and applications in automotive and transport region and agriculture and horticulture sector (Fig. 8b). With a view to regional improvement, Asia remains major manufacture hubs with above 50% of biopolymers currently have been produced (Fig. 8a). Twenty percent of the production capability is located in Europe. This portion is expected to grow to up to 25% by 2022, with the European Commission's commitment to the transition to a circular economy model estimated to speed up the momentum of progress and development of the biopolymers manufacturing in Europe. The land used to cultivate the renewable feedstock for the fabrication of biopolymers around 0.82 million ha in 2017, which accounted for less than 0.02% of the complete agricultural area of 5 billion hectares, 97% of which were used for pasture, feed, and food. Despite the market growth predicted in the next five years, the land use share for biopolymers will remain about 0.02%. Hence, this obviously indicates that there won't be competition among the renewable feedstock for food, feed, and the making of biopolymers [32].

5 Biopolymers in Indian Scenario

5.1 Strategies of the Biopolymer in India

End-use Segments of Biopolymers

Biodegradable and long-lasting products

Cell phone cover, interiors of automotive like seats, headrests, or armrests.

Biodegradable and short-lived products

- Disposable catering package goods
- Packaging
  - Trays and punnets for vegetables, fruits, meat, and eggs
  - Shopping bags
  - Compostable waste collection bags
  - Styrofoam replacement and shrink wraps.
- Medical applications
  - Implants such as screws, pins, or plates
  - Material for pills and capsules.

Emerging End-use Segments of Biopolymers

- 3D printing
- Toys and teethes
- Children feeding bottles
- Metalized biaxial oriented—PLA for food packaging
- Polymer films in sanitary napkins/diapers
- Microbeads from bio-based and biodegradable polymers.

Drivers for the Biopolymers Market Growth in India

Wide ranges of significant drivers are triggering the growth of the biopolymers market universal. A lot of these are associated in Indian context too.

- Mandates and regulations
- Increasing eco-awareness among consumers
- Corporates focused on sustainability
- Technology stabilization
- Cost-effective.

Challenges for Biopolymers

Biopolymers appearance is serious tasks before they achieve large-scale market penetration

- Biopolymers are costly than conventional polymers (could be 3–4 times as costly).

- Upstream technology is still developing, and hence, there are uncertainties in technologies.
- Alternatives—some of them authentic and some not so authentic substitutes—also existing competitive challenges to adoption of biopolymers in numerous mainstream.
- Customer awareness—lot of misconceptions—result in a poor and sometimes misunderstanding of the market, subsequent in delays in investment decision-making.

5.2 Can India Flourish Biopolymers?

Polymers have been an essential portion of our lifecycle. From the beginning, usual polythene bags for fetching groceries to encase of a technology gadget, the polymer is used universally. A current review displays that India is the third major polymer consumer in the world, with entire utilization of polymers of almost 4 million tons and a consequent waste production of around 2 million tons.

Implementation of complete ban on polymer bags is uncertain; on the other hand, we could realize that cities like Bangalore, Chennai, Delhi, Mumbai, Karwar, Tirumala, Vasco, all have executed a ban on polythene bags. In recent years, the usage of polythene bags in Srinagar and other portions of the Kashmir have been created a finable offense. The polymer is an organic repeating unit that has mutually good and bad effects on surroundings, which is why we want to search for a better substitute to it. The other survey says around 1.27 billion individuals use and dispose of polymers nearly every day [33].

The Central Pollution Control Board (CPCB, India) have published report that extrapolated data from 60 Indian major cities and reported by Shreeshan and Ishan [34], Rajit and Kiran [35], the country produces about 25,940 tonnes of plastic waste per day the details are listed in Table 2. About 94% of this consists of a thermoplastic, such as polyethylene terephthalate (PET) and polyvinyl chloride (PVC), which are recyclable. Residual pertaining to thermoset and another kinds of plastics, such as sheet molding compound (SMC), fiber-reinforced plastic (FRP), and multi-layer thermocol, is non-recyclable. On the other hand, volume of plastic waste produced looks like doubtfully low while compared with data of Plastindia Foundation a body of major associations, organizations, and institutions associated with plastics. The Foundation appraisals that during 2017–2018 India consumed 16.5 million tonnes of plastic. Worse, as maintained by industry body Federation of Indian Chambers of Commerce and Industry (FICCI), 43% of India's plastics are utilized in packaging and are single-use plastic. A modern research shows that over 90% of total plastics that end up in the ocean come from rivers in Asia and China. It recognizes the Ganga and Indus as the major source of South Asia.

Biopolymers have been generated from numerous raw materials like vegetable fats and oils, corn starch, pea starch, or microbes. Recently, researchers have been finding that biopolymers could also be produced from microalgae (Sect. 7) and banana

Table 2 Indian major cities generated plastic wastes: Sources Consolidated Guidance for Segregation and Collection and Disposal of Plastic Waste, CPCB September (2017), Shreeshan and Ishan [34], Rajit and Kiran [35]

Cities	Plastic waste (tonnes per day)	Plastic waste (% of municipal solid waste)
Srinagar	28.14	5.12
Jammu	21.68	7.38
Amritsar	24.42	4.44
Shimla	2.23	4.45
Chandigarh	8.18	3.1
Dehradun	14.66	6.67
Delhi	408.27	10.14
Faridabad	79.03	11.29
Agra	40.89	7.86
Lucknow	70.84	5.9
Jaipur	15.58	5.03
Kanpur	106.66	6.67
Patna	12.6	5.73
Guwahati	10.27	5.04
Varanasi	25.92	5.76
Bhopal	23.08	6.59
Dhanbad	7.52	5.02
Shillong	5.27	5.44
Ahmedabad	241.5	10.5
Raipur	23.76	10.61
Ranchi	8.29	5.92
Agartala	5.83	5.71
Surat	149.62	12.47
Kolkata	425.72	11.6
Mumbai	408.27	6.28
Hyderabad	199.33	4.75
Bhubaneswar	31.92	7.98
Pune	101.35	7.8
Vijayawada	43.72	7.29
Chennai	429.39	9.54
Bengaluru	313.87	8.48
Puducherry	26.46	10.46
Coimbatore	66.3	9.47
Kavaratti	0.24	12.09

(continued)

Table 2 (continued)

Cities	Plastic waste (tonnes per day)	Plastic waste (% of municipal solid waste)
Thiruvananthapuram	15.06	6.02
Kochi	9.43	6.29
Madhurai	22.77	5.06
Pune	101.35	7.8
Nagpur	45.96	7.07
Allahabad	18.86	5.39

Average plastic waste generation in India (tonnes per day)—4059.18
Average plastic waste share in municipal solid waste in India—6.92
25 states and union territories have tried to regulating their plastics use in the past two decades

Table 3 Major differences between polymers and biopolymers

Polymers	Biopolymers
Hydrocarbons	Microbes
Eating fossil fuels and releases CO_2	Releases very less CO_2
Non-biodegradable and damages environment	Biodegradable so harmless
Hard to accumulate polymer waste and demolish	Facile to compost locally and destroy
Tremendous versatile in manufactured goods	Very few versatile in product
Low manufacture price	Higher production cost
Simply available	Availability not widespread

peels. As long as these biopolymers are generated from renewable biomass sources, they degrade earlier in environment and release low-level greenhouse gases. They are maintainable as they create very less CO_2 emissions and decrease the consumption of fossil fuels. As discussed in the previous section, the cost of biopolymers production is significantly more luxurious than conventional polymers; they provide better features and advantages over polymers that are made from crude oil. The major difference between polymer and biopolymer is shown in Table 3.

Generally used biopolymer feedstocks are: cellulose, starch, glucose, and vegetable oil. Particular procedures are engaged to alter feedstocks into thermopolymer starch, polylactic acid, poly-3-hydroxybutyrate, polyamide 11, and biopolyethylene. Manufacture of biopolymers is a full-fledged downstream process. For example, while starch is utilized as feedstock, it is place through a scarification method using enzymes to yield liquid glucose. Then liquid glucose would be agitated by special bacteria to create the lactic acid monomer, which is then polymerized to PLA, which are biodegradable polymer [36].

Strategy in India

Last two decades, 25 of the 29 states and several union territories have attempted to control the consumption of plastics. India's first effort at handling the hazard of plastic

waste came in 2011 when the government notified the Plastic Waste (Management and Handling) Rules, 2011. The procedure sought to disincentivize the consumption of poly bags by setting up a costing mechanism for them and also to launch the rules for recycling by local experts. The rules were substituted with a stronger Plastic Waste Management Rules, 2016. The new rules and regulations highlighting on a thorough ban on plastics lower than 50 μm, diminish the usage of multi-layered plastics and hosting extended producer responsibility (EPR) for producers, importers and brand owners to guarantee environmentally sound management of plastic materials up to end of their survives.

Do we have solutions?

Waste-to-energy (WTE) technology incinerates metropolitan waste to generate energy that has been beaten as a clarification to the huge problem. Not only from some state governments, central government also planned to capitalize in 100 WTE technologies by 2020. Since India's waste has high organic content, its calorific value is usually lower than what is necessary to run WTE plants or to make WTE plants effective, plastic content with greater calorific values has to be improved in the municipal waste. The alternate solution is to encourage substitute for polythene bags. That is why last 15 years; bioplastics have been promoted as potential alternatives. They are categorized as oxybiodegradable plastics, hydro-biodegradable plastics, and just biodegradable plastics. Researchers question the actual extent of disintegration of such plastics in landfill environments and their suggestions on food security since edible starch and vegetable oil are used to produce some kinds of biodegradable bags. The new part of research that has motivated enthusiasm is the discovery of plastic-eating bacteria, but what is lost out in revealing such discoveries is often just as dangerous as what is retained. The Indian railway has installed recycle machines at most of the cities railway station to crush the plastic bottles and avoid plastic wastage at the station. The key objectives of installing these machines are to create an environment-friendly initiative, create awareness about the advantage of recycling, and ensure 100% recycling. These machines accept only plastic bottles to recycle. The recycled bottles will be delivered to the fiber-manufacturing companies to be used for clothes, carpets, dustbin cabinet, and grocery bags, etc.

Professors from IIT Madras, Tamil Nadu, India, have established a solar-power scheme to transform non-recyclable polymer into fuel that can replace the diesel used in generators, furnaces, and engines. The technology consists of a mobile unit that would collect and process the excess and currently yields around 0.7 L of fuel oil per kg of polymer/plastic. The mechanism of plastic to fuel comprises a process called pyrolysis—a thermochemical treatment that exposes the material to a high temperature in the absence of oxygen, leading it to go through physical and chemical changes. This produces a low-density fuel oil by fragmenting the polymer chain of plastic at temperature of 350–500 °C. These products can be used as an additional for diesel to power generators, furnaces, and engines. The per capita ingestion in India is still low compared to more developed nations. As per FICCI, Indians consume 11 kg of plastic per year in comparison to 109 kg by an average American. However, this number is predicted to rise in the future. The solution to India's issue with plastic

waste can be addressed via select investments in recycling and confirming effort to cut down on plastics consumption.

5.3 Present Status of Biopolymers in India

Biopolymers are in their budding stage in India with a small number of market companies functioning in this section. Presently, the Indian biopolymers market is plagued by encounters such as less awareness that is typical of developing markets, exclusively the markets business methods with eco-friendly yields; however, there is a prospective for companies desiring to enter the market. The market contributors can demand tax exceptions and procedures that directive use of biopolymers for definite applications. Not only from government support and growing greater environmental awareness, biopolymers industrialists could welfare from the easy accessibility of plentiful feedstock in India. Environmental responsiveness and encouraging the long-term advantage of biopolymers are a preliminary stage that wishes to take to fetching this modification.

Jammu & Kashmir (J&K) is having devoted biopolymer industrialized capability with capacity of 960 metric tons per year. The J&K Agro Industries Ltd has begun its combined venture with Earth Soul India to unveiling the country's first desegregated biopolymer provision that can produce 100% biodegradable and compostable yields. In the market, not only biopolymers, other eco-friendly products which function the same motive. Today, nearly all the stores have substituted polymer bags with jute, cloth, paper, and wicker bags. Biopolymers are biodegradable which are obtained from replenished and natural feedstocks that can be decayed into the earth and also gift to healthier rural and urban economies. These benefits create it perfect the need of biopolymers to adopt severely by Indians. It is up to every human being to fetch a change and stop dangerous ritual of using plastic.

6 Other Medical, Biomedical, Orthopedic, Drug Delivery Applications

Biopolymeric material has a major impact on today's healthcare technology. Drug delivery systems are used to deliver on target, diseases, ailments, and unhealthy body. In the field of smart drug delivery, polymeric systems and nanomaterials play a significant role because they serve as carriers for sending therapeutic agents directly into the intended site of action, with superior efficacy, and no adverse or toxic effects. Polymers are extensively used as biomaterials due to their promising properties for example good biocompatibility, relatively easy design and preparation, a range of structures and exciting bio-mimetic character. In the field of smart drug delivery, polymers play an important role because they serve as carriers for sending therapeutic

agents directly into the planned site of action, with superior efficacy, and no adverse or toxic effects.

Biopolymers and their nanocomposites have made tremendous progress as a result of their biofunctionality, biocompatibility, and biodegradability. These attributes make them resorbable while they serve as a vehicle for drug delivery for healing, skin regeneration, and skin grafting. Biopolymer materials that have been developed for this purpose are hydrolytically sensitive biocellulosics, furan-based polymers, polyesters and their amides, polypeptides, polysaccharides, polyphosphazenes, polyanhydrides, polyurethanes, and pseudo-polyaminoacids. These polymers may be synthesized into hydrogels, spun into fibers and fabricated into fibrous scaffolds, for medical applications. The technology as it evolves tends to seek ways of achieving drug delivery for living cells replication by serving as drug carriers. The drugs may be synthetic nanoparticles or sourced from natural and renewable materials such as metabolic extracts, antibiotics, antiseptics, and antimicrobial drugs from medicinal plants which may be encapsulated into the resorbable biopolymer. The future holds interesting promises for this class of polymers in the areas of biomedicine, skin grafting, wound healing, and regeneration. These materials may be introduced into biological systems by surgical procedures or grafting techniques. With the proven efficacy of this technology, more researches will definitely be carried out on biopolymer materials and their nanocomposites for regenerative and reconstructive medicine. The use of polymers as biomaterials has been the topic of powerful investigation over the past fifty years [37].

7 Few Recent Research Activities of Biodegradable Polymers

7.1 Biodegradable Water Bottle from Algae

Most of the polymer bottles that are produced end up in landfills and the oceans rather than being recycled. It can take centuries for these materials to degrade. Ari Jónsson from the Iceland Academy of Arts has created a neat alternative a biodegradable bottle made out of algae [38]. It remains solid while the liquid is inside, but begins dissolving as soon as it is empty. The bottle is composed of agar, which is derived from the cell walls of red algae. These cells have double-walled structures, with the outer layer containing polysaccharides [39, 40] called agarose and agaropectin. These long chains of sugar molecules are also the basis of agar, a gel-like material that is used as a growth medium in microbiological research and in food preparation.

Combining the algae cell wall material with water allows the gel to be molded into the bottle shape as shown in Fig. 13. It is completely natural and non-toxic. When the algae bottle is empty, the gel dries out and begins to crumble as the polysaccharide bonds come apart. The agar bottle also remains naturally cool in warm temperatures, which might be a nice bonus. That does not mean it is ready for use in a real product.

Fig. 13 Different stages of degradation of algae/polysaccharides and chemical structure of polysaccharides [38]

The algae bottles are not very durable, and their shelf life is still an unknown. It might also encourage bacterial growth in a way that the polymer does not [38] [41]. It is a cool design, though maybe not the most practical. Still, the author can address the overuse of polymer, the better.

7.2 'Infinitely' Recyclable Plastic

As suitable as it is, the polymer is not the most eco-friendly material. Our regular use of the stuff has seen enormous amounts of it lodged in Arctic sea ice, penetrating to the deepest parts of the ocean and even traveling up the food chain. To try to discourage us off it, chemists [42] at Colorado State University have now established a polymer that apparently has all the advantages, but can be easily broken down and recycled over and over. The new polymer is designed to be as versatile as polymers in everyday use, meaning it is lightweight, heat resistant, strong, and tough. The difference is that it is far easier to recycle than conventional polymers, which require toxic chemicals or complicated procedures for diminishing returns. Its monomers can be polymerized at ambient temperature in a matter of minutes, with little amounts of a catalyst and without solvents. It is chemically biodegradable, planned to easily break down into its monomeric state a reaction with a catalyst. It can then be re-polymerized without needing to be disinfected first.

7.3 Newly Discovered Plastic-Eating Bacteria

Recently, Japanese scientist discovered a microorganism that consumes plastic. Now, the bacterium, called as *Ideonella sakaiensis*, has been confirmed that entirely breaks down the common type of plasticlike polyethylene terephthalate (PET) used in bottles and other vessels. Such kind of plastic creates up a huge percentage of all the plastic waste in the world, especially in the ocean, and today, scientists are considering

whether the hungry little bug could be used to recycle such polymer and reduce pollution.

The bacterium uses a couple of enzymes to disconnect the PET and turn it into a food source—much the same as the way other animals' bodies use enzymes to break down other types of food. Problem is it takes up to six weeks for the bacterium to totally breakdown a small, low-quality sample of PET. Microbiologist Kohei Oda of the Kyoto Institute of Technology co-authored the research work published in Science journal [43], and he was "very surprised to find microorganisms that degrade PET" because plastic has constantly been thought to be non-biodegradable. During their examination of 250 PET samples collected from recycling facilities in Osaka, Japan, the experts were observing for evidences to describe how the plastics broke down over time.

PET has the highest recovering rate of all plastics, yet approximately half the plastic goods produced by PET are not recycled. PET is common in single-use water flasks, but also in another food packaging like clear salad containers, peanut butter jars, and potato chip bags. Other scientists reviewing plastic degradation are paying consideration, as this breakthrough may be the first step in a lengthy journey to addressing the huge issue of ocean plastic.

8 Conclusions

The increasing demand for environmental and waste management policies globally has motivated the researchers to focus on the development of green polymers from a renewable resource like biopolymers in order to protect the environment. The release of polymers as waste materials generated a significant problem for the environment after service life. Earlier, many of the packaging materials used in the food industry are non-biodegradable. Disposal of these materials after use is a major concern; most of them take hundreds of years before finally decomposing. The better way to deal with this issue is keep away yields that produce waste materials that take more than a year to decay in landfills through a proactive plan from natural materials. Disposing of massive quantities of wastes generated by non-biodegradable polymer paves ways for the study of biopolymers as alternative materials.

The recent trend in food wrapping is the use of composites of diverse polymers like starch-PLA blends, starch-PCL blends. Bottles, jars, vials; drums, pails, cans, barrels, buckets; caps, closures, aerosol parts, wrapping film, food vessels, disposable cups; coating for all types of packing, domestic and institutional waste bags and film; boxes and baskets, etc., are being factory-made by using biodegradable polymers. The use of biopolymer/polymer bionanocomposites as drug carrier is majorly attributed to their biodegradability, versatility, and broad range of properties. The future holds interesting promises for this class of polymers in the areas of biomedicine, skin grafting, wound healing, and regeneration. These materials may be introduced into biological systems by surgical procedures or grafting techniques. With the proven efficacy

of this technology, more researches will definitely be carried out on biopolymer materials and their nanocomposites for regenerative and reconstructive medicine.

Nowadays, authorities globally are encouraging people to employ more green materials from renewable resources. One could still expect that the price of biodegradable polymers, especially those produced from natural sources to decrease in the coming years to ensure that biodegradable polymers can replace traditional polymers. This can simply solve a huge problem that we are currently facing with regard to waste disposal of traditional polymer-based materials.

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Chapter 2
Green Polymer Composites Based on Polylactic Acid (PLA) and Fibers

Mokgaotsa Jonas Mochane, Teboho Clement Mokhena, Emmanuel Rotimi Sadiku, S. S. Ray and T. G. Mofokeng

1 Introduction

In the past years, biomaterials prepared from renewable resources have attracted a lot of attention in both the academic and industrial sectors [4]. The use of biomaterials maintained an increase of more 10% every year, which shows the need and widespread of these materials [69]. The introduction of biomaterials generally improved the living standard of humans to a higher level. There are three classes that are normally used as biomaterials which include a single ingredient or in many cases a composite ingredient [69]. In comparison with metal and ceramic, polymers are advantageous because they offer organic matrix and its molecular weight is easy to control [69]. There are two distinguished categories of polymers, i.e., biodegradable and non-biodegradable polymers. Biodegradable polymers are a specific type of

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polymer that breaks down after its intended purpose to result in natural by-products such as gases (viz., carbon dioxide and nitrogen), water, biomass, and inorganic salts. Hence, biodegradable polymers are environmentally friendly and mostly used for many applications due to their excellent degradation behavior and for the purpose of environmental protection [69]. Biodegradable polymers can further be differentiated into naturally derived and synthetically prepared polymers. Synthetic polymers include esters, amide and urethane or polymers with carbon backbone in which additives such as antioxidants are added [78]. Among synthetically prepared biopolymers, saturated poly-α-hydroxyl esters [viz., polylactic acid (PLA)] are frequently used in many applications, including the biomedical application [64]. Under normal environmental conditions, PLA can degrade into carbon dioxide and water as well as methane over a period of months to more than a year which is a distinct advantage compared to other commodity polymers that need prolonged periods [4]. Polylactic acid (PLA) is linear polyester obtained from renewable resources such as corn, sugar, potato [2, 39, 38]. There are three kinds of PLA which include poly(D-lactic acid) (PDLA), poly(L-lactic acid), and racemic blend D,L-PLA (PDLLA) based on various microstructures [69]. PLA is widely used in biological areas and packaging applications because of its excellent compatibility, bioabsorbability, and degradation mechanism in human bodies. However, neat PLA is unable to meet all the requirements for specific applications. Furthermore, PLA production has been limited due to its high cost. Therefore, the incorporation of fibers into PLA not only can reduce the amount of PLA required but also produces composites with a wide range of applications. A lot of studies have investigated the performance of PLA with different types of fibers to improve its mechanical and thermal properties [21, 49, 74, 79, 83]. The aim of this chapter is to report on the state of the art of PLA-based composites with natural fibers for the production of eco-composites.

2 Fiber Selection for Reinforced PLA Green Composites

The type of fiber is distinguished by its origin, i.e., either from plants or animals and/or even minerals. It is well known from the literature [8, 30, 37] that all plant fibers contain cellulose as their main component, while animals have protein as their major structure. In the past, mineral-based fibers which include asbestos have been employed as reinforcement in composites. However, these types of fibers are avoided because of health issues which include carcinogenic through inhalation or ingestion. It has been heavily reported [24, 28, 30, 37, 81] in the literature that plant fibers have higher strengths and stiffness in comparison with the available animal fibers. Hence, this makes plant fibers more suitable for the formation of composites and as a result this chapter focus on natural fibers reinforced composites, known as "eco-composites".

3 Types of Fibers

3.1 Natural Fibers

The popularity of natural fibers is undeniably based on the fact that natural fiber is not only good for the skin, but also good for the environment. Natural fibers are classified into an animal (wool and silk), mineral (asbestos), and plant/vegetable (leaf, seed, wood, and grasses). Natural fiber consists of a primary cell wall, three secondary cell walls, and a lumen surrounding the whole structure, resulting in a rounded, elongated hollow cross-sectional structure (Fig. 1). The primary constituents of any natural fiber are hemicelluloses, cellulose, pectin, and lignin. The percentage of these components of natural fiber is different and varies with the type of fiber (Table 1). The most commonly used natural fibers in polymer composites are flax, hemp, jute, kenaf, sisal, and bamboo fibers [29, 37] which all originate from the plant.

3.2 Bamboo Fiber

Bamboo fiber is a woody evergreen plant in the grass family Poaceae. The most important characteristics that make the majority of bamboo distinct from other grasses are their woody perennial habit and peculiar flowering and seeding behavior [54]. It has two distinctive areas called nodes and internodes along the length. It is worth mentioning that the distance between the nodes is different depending on the type

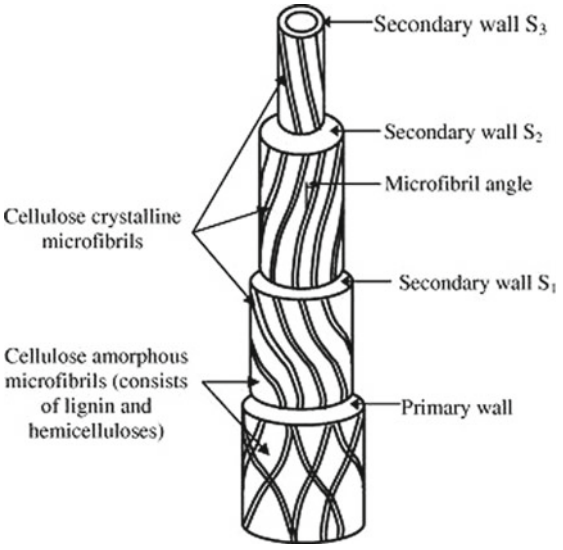


Fig. 1 Structure of natural fiber Kabir et al. [29]

Table 1 Constituents of some of the selected natural fibers [1, 22, 34, 75]

Fiber-type	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Pectin (%)	Wax (%)	Ash (%)	Microfibrillar angle (°)
Abaca	53–63	7–9	20–25	–	3		20–25
Bamboo	26–43	1–31	30	–	10	–	–
Banana	63–83	5	–	–	11	–	11–12
Coconut							
Coir	36–43	0.15–0.25	41–45	3–4	–	–	30–49
Cotton	83–91	–	3	0.6	8-9	–	–
Flax	64–72	2–2.2	64–72	1.8–2.3	–	–	5–10
Hemp	70–74	3.7–5.7	0.9	0.8	1.2–6.2	0.8	2–6.2
Kenaf	45–57	22	8–13	0.6	0.8	2–5	2–6.2
Sisal	78	8	10	–	2	1	–

Table 2 Global production of sisal fiber

Country	Tons/per year
Brazil	130,000
Mexico	45,000
China	36,000
Tanzania	24,000
Kenya	25,000
Madagascar	15,000

of bamboo. Bamboo has been used in different applications such as building construction, housing, flooring, automotive, and furniture due to its low density, good mechanical properties, and low cost [60].

3.3 Kenaf Fiber

Kenaf is one of the most used fibers as reinforcing filler in polymer matrix composite. It is herbaceous that produces more 3 m of the species within 3 months under ambient conditions [41]. The production of kenaf plant depends on different conditions such as cultivar, planting date, photosensitivity, length of growing season, plant population, and plant maturity [41]. It is reported that the stem of kenaf does not have branches; as a result, it is built up of an outer layer of bark (30% contribution) and a core (60–70% of the weight) [41]. The core is an isotropic and amorphous, whereas the bark has an oriented high crystalline fiber pattern [5]. Kenaf fiber is used to make high-grade pulps for the pulp and paper industry, composite boards, or textiles. Furthermore, animal bedding, sorbents, and horticultural mixes use short core fibers.

3.4 Sisal Fiber

Sisal fiber is a hard fiber derived from the leaves of the sisal plant known as Agave sisalana. In order to obtain the sisal fiber, the leaf of the sisal plant is crushed between the rollers and then mechanically scraped. The fiber is washed and dried, either mechanically or by natural means. Furthermore, after drying the fiber, it is double brushed to obtain the lustrous strands, creamy white in color, with an average length of 120 cm and 0.4 mm in diameter. The fiber is used in many applications because of its good strength, durability, and resistance to deterioration in saltwater. Table 2 illustrates the world largest production of sisal fiber.

Table 3 General properties of jute fiber [45, 46]

Type of property	Jute fiber
Cellulose (%)	61–71.5
Hemicellulose (%)	12–13
Lignin (%)	13.6–20.4
Pectin (%)	0.2
Waxes (%)	0.5
Moisture regain (%)	12.6
Bulk density (kg/m^3)	1300–1500
Fiber length (mm)	0.8–6
Diameter of fiber (μm)	5–25

3.5 Jute Fiber

Jute fiber is an important agricultural product. It is the cheapest vegetal bast fiber which is found in abundance in Bangladesh and India [45]. Jute is a bast fiber which belongs to the Tiliaceae family. To obtain jute fibers, jute plant is normally cut and kept immersed in the water for the retting process during the season. Furthermore, both inner and outer stems get separated and the outer plant gets separated to form fibers. Jute plant takes about 2 months or more to grow to a height of 12–15 ft. Traditionally, jute fiber is used to make hessian clothes, ropes, shopping bags, and floor mats. Jute fiber just like any other natural fiber has many advantages such as low cost, eco-friendly, and fairly good mechanical, which makes it a suitable candidate for the replacement of synthetic fiber. The chemical composition and physical and mechanical properties of jute fiber are given in Table 3.

4 Matrix Selection for Biopolymer Composites

It is well documented in the literature [27, 58] that a matrix, irrespective of its type, plays a significant role in the preparation of composites, in this case, fiber composites. It keeps the fibers in the proper position and provides resistance against extreme environmental conditions, such as chemicals and moisture. Furthermore, the matrix transfer stresses to fibers and protects them from mechanical degradation. Currently, polymers have replaced a lot of traditional host matrices because of their advantages which are light in weight, high specific strength, easy processing, and the productive and low cost in the market. There are two distinguished types of polymers which are used as host matrices, i.e., biopolymer and synthetic polymers. Synthetic polymers are human-made polymers and can be classified into four main types: thermoplastics, thermosets, elastomers, and synthetic fibers. However, biopolymers are polymers produced by living organisms. The society at large is heavily depending on non-

renewable fossil fuels, such as petroleum and coal; however, the products made from these materials cause environmental pollution which makes their development and utilization to be reduced [7]. Therefore, it is very important to find green materials that can replace petroleum-based products to decrease the utilization of petroleum and coal which happen to harm the environment. Recently, the idea is to develop bio-based composites in an industrial application with the aim of reducing the use of fossil energy to the natural environment, but also achieving green composites. It is clear that the preferred matrix for natural fibers would be the biopolymer in comparison with synthetic polymers. Polylactic acid (PLA) possesses high strength, good processability, and excellent mechanical properties. Compared with the well-known commodity polymers such as polyolefin and other petroleum-based plastic, PLA is biodegradable which belongs to the green type of matrix, non-polluting material [32, 31]; as a result, it makes PLA a matrix of choice for renewable and non-polluting fillers for the formation of green composites.

5 Characterization

5.1 Morphology (Unmodified and Modified Composites)

Natural fibers blended with biodegradable polymers appear to be the best candidates for the preparation of smart green composites for a different application. There are different types of natural fibers (viz., wood, bamboo, banana, jute, hemp, sisal, even extracted cellulose) that have been added to the PLA matrix for designing of green composites. The morphology of the PLA/natural fiber composites was affected by the treatment, type, and content of fiber used. Generally, irrespective of the type of fiber added to PLA, untreated fiber in most cases showed number of fiber pull out from the PLA matrix (Fig. 2a and b) [43]. This is due to a weak interfacial bonding of the fiber and PLA matrix. The presence of hydroxyl groups and other polar groups in natural fibers plays a significant role in making them hydrophilic, leading to incompatibility and poor wettability with hydrophobic matrix [42].

It is evident that there is a problem with the interface of the natural fiber and PLA. The fiber–matrix interface is the area in which the two phases are chemically and/or physically merged. Interfacial adhesion plays a major role in terms of determining the final properties of composites [29]. Poor interaction between the fiber and matrix resulted in poor overall properties of the composites. Several approaches were done to improve the interfacial adhesion between PLA and natural fibers. One of the well-known methods of improving the interfacial adhesion between the matrix and filler is through the addition of compatibilizer, chemical treatment, and reactive additives [29]. Chemical treatment resulted in more reactive groups on the surface of the fiber and facilitates effective bonding with the matrix. Li et al. [43] investigated the effect of sisal fiber surface treatment on properties of sisal fiber-reinforced polylactide composites. In their study, the authors treated sisal fiber with MPS-g-PLA (polylactide-

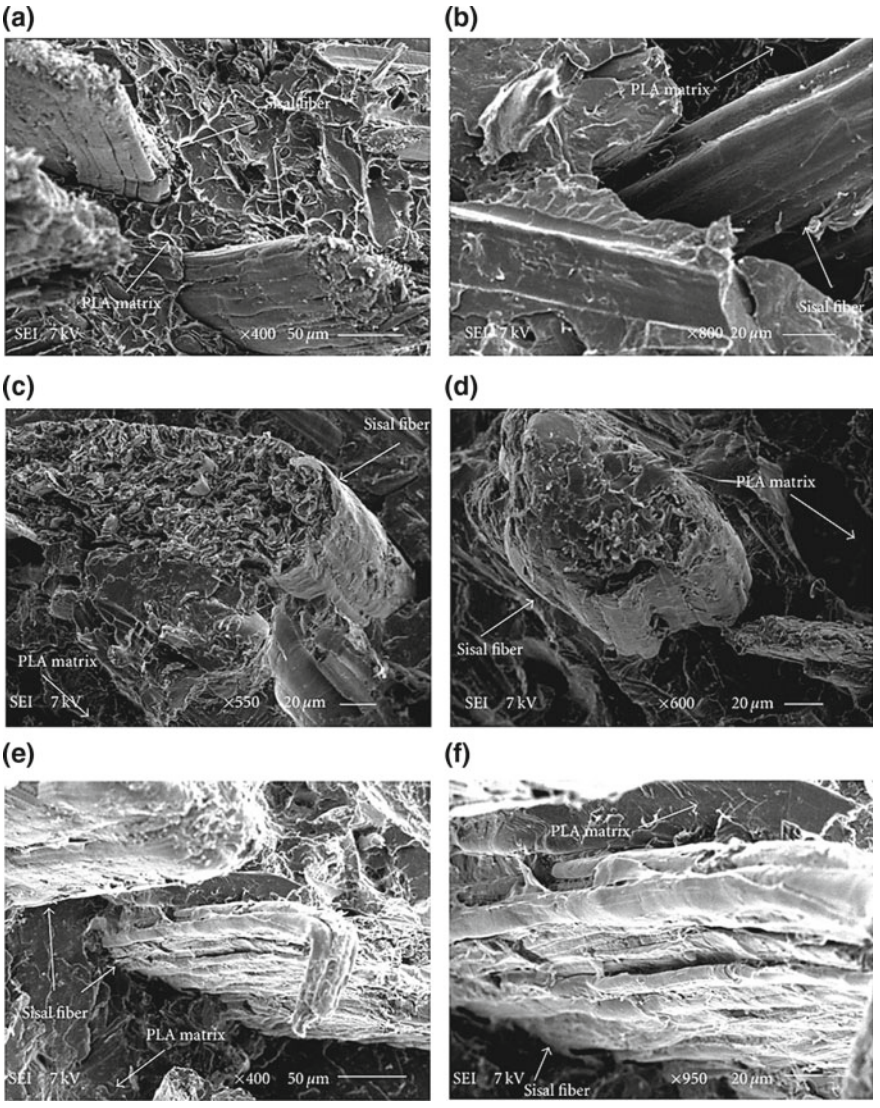


Fig. 2 Morphology of a fractured surface of 30 wt% sisal fiber/PLA composites. **a**, **b** Unmodified sisal fiber; **c**, **d** sisal fiber modified with PLA-co-PGMA; **e**, **f** sisal fiber modified with MPS-g-PLA Li et al. [43] Open Access

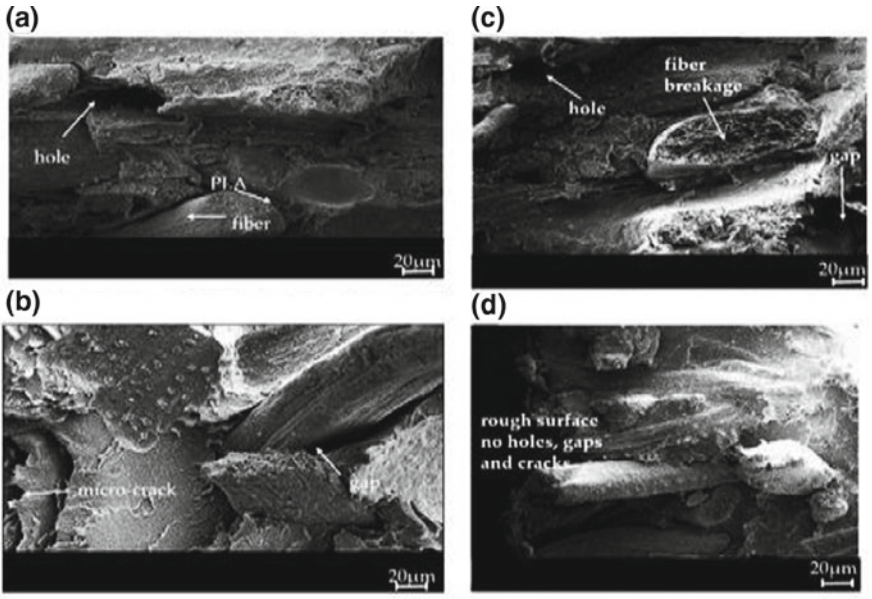


Fig. 3 Morphology of fractured surfaces of **a** EFBF-KCF-PLA, **b** BR (EFBF-KCF)-PLA, **c** EFBF-KCF-MAPLA, and **d** BR (EFBF-KCF)-MAPLA Birnin-Yauri et al. [7] Open Access

graft-γ-methacryloxypropyltrimethoxysilane) and PLA-co-PGMA (polylactide-co-glycidyl methacrylate). It is noted in Fig. 2c–f that the sisal fibers were strongly connected with PLA, which suggested that the interfacial bonding between sisal fiber and PLA was improved with the treatment of the fiber. The interfacial adhesion between the natural fiber and PLA may be improved better by the synergistic effect of filler and PLA treatment. Birnin-Yauri et al. [7] investigated the effect of maleic anhydride (MA)-modified polylactic acid melt-blended with aqueous borax (BR)-treated hybrid oil palm empty bunch fibers/kenaf core fibers. The authors reported that a hybrid system, i.e., [BR (EFBF-KCF)-MAPLA] which consists of fibers and PLA treatment, showed rough surfaces with no holes, microcracks, or even gaps (Fig. 3d) due to a better interfacial adhesion provided by BR-treated hybrid fibers and compatibilization effect provided by the MA-modified PLA.

5.2 Mechanical Properties of PLA/Natural Fiber Composites (Unmodified and Modified)

There are several factors that affect the mechanical performance of natural fiber-reinforced composites, which include fiber selection, interface strength, fiber dispersion, porosity, and fiber orientation [57]. Usually, high performance is obtained from

Table 4 Mechanical properties of selected natural fibers [9–11, 13, 14, 65, 19–20, 25, 40, 47, 48, 59, 56, 57, 63, 70, 88, 92]

Fiber-type	Failure strain (%)	Tensile strength (MPa)	Young modulus (GPa)	Length (mm)
Ramie	2.0–3.8	400–938	44–128	900–1200
Sisal	2.0–2.5	507–855	9.4–28	900
Cotton	3.0–10	287–800	5.5–13	10–60
Hemp	1.2–3.2	550–1110	58–70	5–900
Jute	1.5–18	393–800	10–55	1.5–120

fibers with high cellulose content and with cellulose microfibrils aligned in the fiber direction. Table 4 depicts mechanical properties of some selected natural fibers. It can be seen that ramie, hemp, and flax are among the cellulose-containing natural fibers with the highest Young's moduli and tensile strength.

The interfacial adhesion between the fiber and matrix plays an important role in the final mechanical properties of composites. Stress is transferred between the fiber and matrix across the interface; as a result, a good interfacial adhesion is needed to obtain prime reinforcement. However, one could take note that there is a huge possibility that a strong interface may facilitate crack propagation which normally decreases toughness and strength. One of the challenges in polymer composites is to fully understand the dispersion and aggregation of fibers in the polymer matrix. A better fiber dispersion may promote good interfacial bonding, reducing voids so that the fibers are fully surrounded by the matrix [23, 57]. Furthermore, it is well documented in the literature [6, 68] that fiber or any filler dispersion can be influenced by processing parameters such as temperature and pressure. The use of extensive mixing process, i.e., twin screw extruder, showed better fiber dispersion. However, the use of such processing techniques in comparison with a single screw extruder damages the fiber and reduces the length of the fiber. One of the factors that have not been taken into consideration is porosity, and it is also known to have an influence on the mechanical properties of composites. It has been noted that there may be an inclusion of air in some cases during processing. This means that lumens and other void features within the fiber bundles may become trapped during the processing of the composites at higher pressures due to the inability of fibers to compact. It was reported in the literature [57] that porosity increases with an increase in fiber content and reduction in mechanical properties thereof. For example, the relationship between compressive strength and void ratio was investigated by Kim et al. [33], who reported a decrease in compressive strength (Fig. 4) with increasing void ratio.

There are a lot of literature which have reported on the mechanical properties of PLA/natural fiber composites [21, 49, 73, 74, 79, 83]. Most of the studies [21, 49, 74, 79, 83] reported on an increase in the mechanical properties (viz., tensile modulus, tensile strength) of the PLA composites with increase in fiber content. However, it was noted that the improvement in mechanical properties of PLA is dependent on the fiber content, whereby it was realized that the increase in fiber content above the optimum

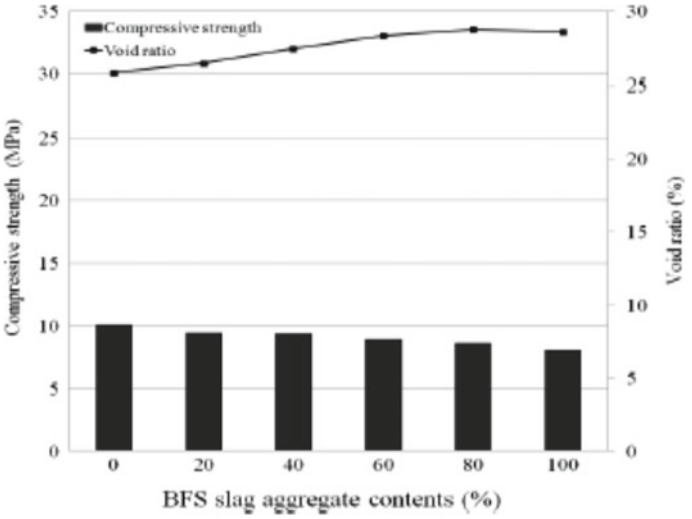


Fig. 4 Relationship between compressive strength and void ratio of porous concrete plant (natural jute fiber) Kim et al. [33] Open Access

content did not have any significant effect on the properties of the matrix [89]. It was also shown that the properties improved further with the treatment of the fiber. The most popular treatment of natural fibers includes alkali, acetyl, silane, and maleated anhydride coupling agent [3]. It is believed that the improvement in mechanical properties of the treated fiber composites was due to a better interfacial adhesion between the fiber and PLA. It is well known that the chemical modification optimizes the interface between the fibers. Chemical coupling agents are molecules which are considered to be processed in two ways: Firstly, they react with the hydroxyl groups of cellulose and secondly their reaction with functional groups of the matrix [62]. Zhang et al. [89] investigated the properties of poly(lactic acid) and different types of natural fibers which include bamboo, wood, and coconut fibers. It was observed by the authors that the addition of three kinds of natural fibers could improve the mechanical properties of the composites and the properties improved further for the treated composites. It is further observed by the authors that the tensile strength of PLA first increased and then decreased with the increase in the fiber content from 1 to 8 wt%, whereby the highest was reached when the fiber content was 2 wt%. The results meant that the strength of PLA was effectively improved by the addition of a certain amount of natural fiber which was below 8 wt% in their case. The authors attributed the improvement in mechanical properties below fiber content of 8 wt% due to the ability of fibers to nucleate PLA, as a result accelerating crystallization which improved the tensile strength of the material. However, with the increase in natural fiber content, there is more aggregation formation leading to defects and stress concentration in the material which made the tensile strength to decrease. Besides the improvement of other mechanical properties' parameters such as tensile

strength and modulus, it was generally found that the elongation at break of PLA decreased with the addition and increasing in natural fiber content. In most cases [89], the decrease in elongation at break was attributed to the nucleating ability of natural fibers which improves the crystallization of the matrix, as a result, decrease the elongation. Table 5 summarizes the mechanical properties of selected studies of PLA/natural fiber composites.

5.3 Flammability of PLA/Natural Fiber Composites

PLA/natural fiber biocomposites are gaining popularity due to their renewability and degradability. However, they have the main limitations for some applications such as poor flammability resistance. There are two forms of products that are obtained upon burning of composites; these are high cellulose content and high lignin content. High cellulose promotes higher flammability, whereas higher values of lignin show there is a greater chance of char formation [67]. The application of PLA/natural fiber composites for flame-retardant applications has attracted attention from researchers due to the environmentally friendly characteristics of these materials. The incorporation of halogen-free flame-retardant fillers in biocomposites results in low toxicity and does not produce large quantities of smoke. The common method used for incorporating flame-retardant fillers is by blending them into composites during processing. Different techniques are used for determining the flammability properties of different PLA/natural fiber flame-retardant composites which include cone calorimeter, horizontal burning, and UL-94 test. According to the previous results [71], PLA/natural fiber composites without any flame-retardant filler do not pass the requirements of UL-94 testing. The addition of flame-retardant filler improved the flame resistance properties of PLA/natural fiber biocomposites (Table 6). The intumescent flame-retardant filler forms an expanded carbonized layer on the surface of the PLA during thermal degradation. This layer acts as an insulating barrier, reducing the heat transfer from the polymer to the flame and also the diffusion of oxygen into the material. In some cases, the treatment of fibers resulted in a decrease in flame resistance properties of PLA (Table 7) composites, especially for alkali-treated PLA biocomposites [71]. The main reason for the decrease in flame retardancy of PLA/natural biocomposites in the presence of alkali treatment is the removal of lignin from fiber surface resulting in a removal of the carbonizing agent, thus leading to a poor char formation [15]. However, the treatment of fibers with a non-chemical method like plasma treatment resulted in better flame resistance properties than the untreated composites. No reason was provided by the authors for such a slight improvement in flammability for plasma treatment.

In other studies [17, 72], the enhancement in flammability resistance of PLA/natural fiber biocomposites was done by the chemical treatment of fiber with a flame-retardant chemical like diammonium phosphate (DAP). In this method, the fibers were immersed in a chemical solution with different flame-retardant chemical concentrations. Suardana and co-workers investigated the fire resistance properties

Table 5 Mechanical properties of some selected natural fiber/PLA composites

PLA/fiber system	Method of preparation	Type of functionalization	Results	References
Kenaf/PLA	Fabricated at a molding temperature of 160 °C		Tensile and flexural strengths increase up to 50% fiber content	Ochi [49]
PLA/sisal, jute, and elephant grass	Injection molding technique	(i) Mercerization process including immersion in 10% NaOH (ii) Alkali-treated fibers added in hydrogen peroxide	(i) Elephant grass at 20% fiber showed higher tensile strength than treated jute and neat PLA (ii) Flexural strength of treated elephant grass at the same fiber content was higher than sisal composite and neat PLA	Gunti et al. [21]
PLA/coir	Co-rotating twin screw extruder and injection molding	Hydrogen peroxide and sodium hydroxide	The tensile modulus of PLA biocomposites was increased by increasing the treated coir fiber content.	Sun et al. [74]
Short jute fiber/poly(lactic acid)	Co-rotating twin screw extruder	Phosphorous-based compound: DOPO and DOPO-ICN	(i) The decrease in tensile modulus of jute/PLA with increasing DOPO loadings (ii) The tensile strength and tensile modulus increased by adding DOPO-ICN above 3%	Yu et al. [83]
Bamboo flour/PLA	Composites mixed for 360 s at 190 °C and 40 rpm, followed by compression molding at 190 °C	PLA-g-glycidyl methacrylate (GMA)	Mechanical properties of the composites prepared with PLA-g-GMA were improved over those of PLA/BF composites without compatibilizer	Wang et al. [79]
Bamboo fiber bundles/PA	(i) Biodegradable PLA was put on the surface of bamboo fibers (ii) Secondly, the biodegradable composite specimen was fabricated by hot press	Effect of molding temperature	(i) The flexural strength of composites increased with increase in fiber content (ii) The flexural strength of composites decreased at a molding temperature of 180 °C	Ochi [50]
(i) Kenaf/coir/PLA, (ii) bamboo/coir/PLA, and (iii) kenaf/bamboo/coir/PLA	(i) Fibers were soaked with the PLA suspension (ii) Dried at room temperature for 24 h (iii) Hot pressing method to obtain a mold		The tensile strength of kenaf/bamboo/coir/PLA higher than bamboo/coir/PLA and kenaf/coir PLA	Yusoff et al. [86]

(continued)

Table 5 (continued)

PLA/fiber system	Method of preparation	Type of functionalization	Results	References
Sisal fiber/PLA	Melt mixer	Alkaline and silane treatments	Alkali-treated and NaOH + silane-treated fibers showed the highest tensile strength values	Orue et al. [53]
Sisal/PLA		Alkali and silane treatment	All treatments decreased the tensile strength values of sisal fibers, especially when the combination of NaOH + silane treatment was used	Orue et al. [52]
Sisal/PLA	Melt blended	(i) Plasticized with vegetable oils (ii) 30 wt% NaOH-treated sisal fibers	70 and 30% improvement in elongation at break and tensile modulus, respectively, for a combination of vegetable oil and sisal fibers	Orue et al. [51]
Unidirectional flax and flax-paper layers/PLA	Composite molding refers to Couture et al. [16]		The results showed the specific tensile properties of the flax/PLA (252 MPa cm^3 g^{-1}) and flax-paper/PLA (217 MPa cm^3 g^{-1})	Couture et al. [16]
Hemp/PLA	Batch mixing	Plasticized with poly(ethylene glycol)	Mechanical tests showed that the modulus of elasticity of the composites markedly increased with the content, reaching 5.2 GPa in the case of crystallized PLA reinforced with 20 wt% hemp, whereas the elongation and stress at break decreased with an increasing amount of fiber for all examined systems	Masirek et al. [44]
Ramie/poly(lactic acid) (PLA)	Fabricated by the compression molding	Ramie plain woven fabrics were pre-treated under wet state by cyclic tensile loading several times	The treated fabric reinforced composites had 35% higher tensile strength, 32% higher Young's modulus, 20% higher flexural strength, and 17% higher flexural modulus than the untreated ones	Zhou et al. [91]

Table 6 Effect of the APP on the flame resistance properties of PLA/kenaf/PEG Shukor et al. [71]

Designation	APP (phr)	LOI (%)
A0	0	27.6
A10	10	29.4
A15	15	30.3
A20	20	31.6

Table 7 Effect of alkali treatment on flame retardancy properties of PLA/kenaf/PEG/APP biocomposites Shukor et al. [71]

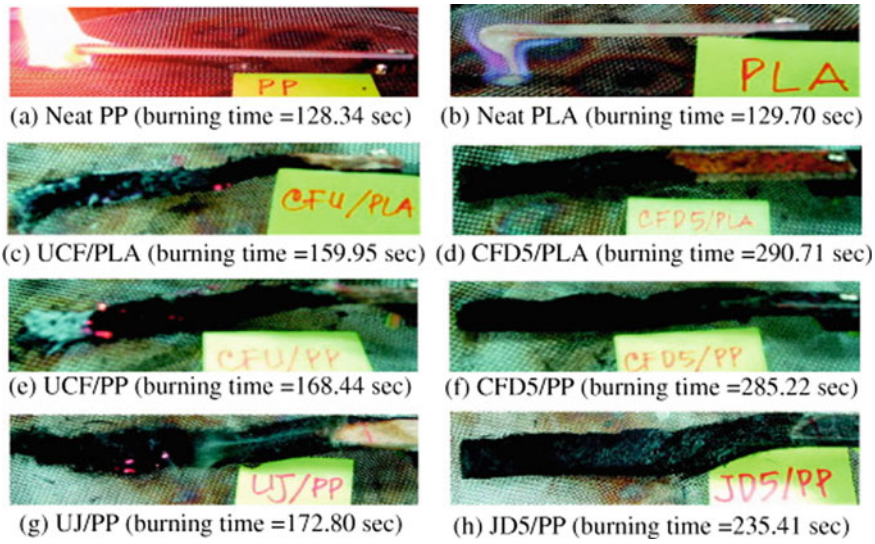
Designation	NaOH (%)	LOI (%)
A10	0	29.4
A10-N3	3	29.0
A10-N6	6	28.4
A10-N9	9	28.0

Table 8 Code representing fiber types used for weaving to natural fiber mat. A = abaca, J = jute and S = sisal

Weft	Warp		
	Sisal fiber	Abaca fiber	Jute fiber
Sisal fiber	S + S	S + A	S + J
Abaca fiber	A + S	A + A	A + J
Jute fiber	J + S	J + A	J + J

of biocomposites using DAP for the treatment of fibers. The flame was applied to the free end of the specimen for 30 s, and the time required to burn a 75 mm length of each specimen (from the first reference mark until the second reference mark) was determined. The authors reported that neat PLA started dripping immediately when it contacted fire (Fig. 5b). The reason for this is probably that heat and flammable volatiles penetrated PLA in the absence of a flame-retardant material, and therefore, no char residues were formed. The addition of fibers, i.e., coconut and jute, into PLA reduced the burning rate and mass rate (Fig. 6), with the rates reducing more in the presence of DAP-treated fibers. The addition of DAP into PLA matrix, therefore, enhances the barrier properties of the char layer so that the heat transfer rate is reduced. According to the authors, a char is formed through the heating of fibers in a DAP solution at a temperature of around 160 °C which led to the formation of phosphoric acid and ammonia. The formed phosphoric acid can phosphorylate the primary hydroxyl group of cellulose to form a phosphorus ester. The ester catalyzes the dehydration of cellulose, whereby they promote the formation of char and water at the expense of levoglucosan.

The effect of natural fiber types and sodium silicate coating on natural fiber mat/PLA composites tensile properties and the rate of fire propagation were investigated by Thongpin et al. [77]. Before weaving, the fibers were treated with 5% NaOH to remove hemicellulose and lignin. In this study, three types of natural fibers, i.e., jute, sisal, and abaca, were plain weaved to fiber mat. Table 8 illustrates the code used for weaving to natural fiber.



(a) Neat PP (burning time =128.34 sec) (b) Neat PLA (burning time =129.70 sec)
(c) UCF/PLA (burning time =159.95 sec) (d) CFD5/PLA (burning time =290.71 sec)
(e) UCF/PP (burning time =168.44 sec) (f) CFD5/PP (burning time =285.22 sec)
(g) UJ/PP (burning time =172.80 sec) (h) JD5/PP (burning time =235.41 sec)

Fig. 5 Pictures of the samples, **a** and **b** polymer during the burning test, **c–h** composites after burning test Suardana et al. [72]

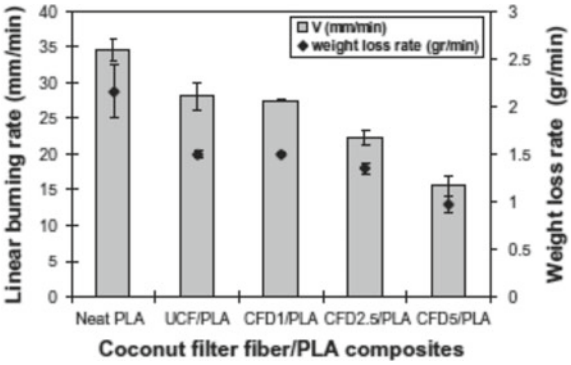


Fig. 6 Linear burning rate and mass rate of coconut filter fiber/PLA composites Suardana et al. [72]

The weaving was performed by hand using a square wooden block fit with nails for weaving using one and two types of natural fibers as weft and warp fiber to produce natural fiber mat. The fiber mat was also impregnated with sodium silicate solution extracted from rice husk ash. Furthermore, the fabric mat and sodium silicate-coated mat were then impregnated with a PLA solution to produce prepreg. Dried prepreg was laminated with PLA sheet using compressing molding machine to obtain natural fiber mat/PLA composite. Figure 7 illustrates the wooden block used in this study for the plain weave to produce a natural fiber mat. The flammability properties of the composites were investigated using UL-94. Neat PLA was burning very fast with dripping, and dripping was reported to carry flame (Fig. 8). However, the authors observed a decreased rate of fire propagation for natural fiber

Fig. 7 Wooden block used for plain weave to produce natural fiber mat Thongpin et al. [77] Open Access

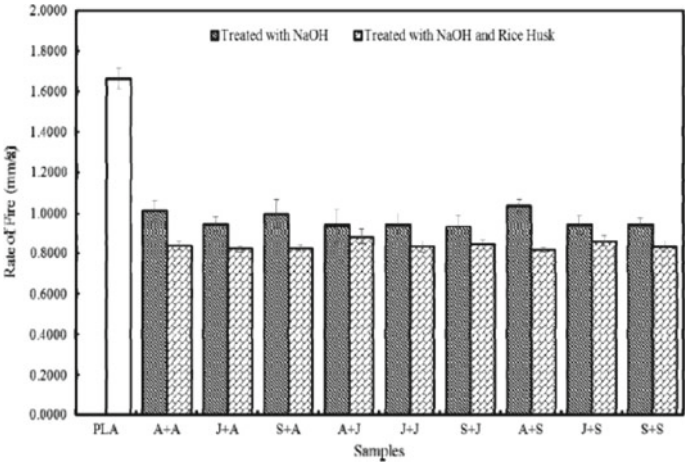


Fig. 8 Rate of fire propagation of natural fiber mat/PLA, hybrid natural fiber mat/PLA, and sodium silicate-treated fabric composite specimen average from 10 specimens Thongpin et al. [77] Open Access

fabric/PLA composites. This was attributed to a lower amount of polymer and also by the presence of natural fibers. Most importantly, it was observed that the type of fiber did not show a significant difference in the fire propagation. After treatment, sodium silicate was deposited on the fabric surface. The improvement was about 17% compared to untreated fabric. This was due to silicate which is widely known for their heat resistance. Silicate material serves to isolate heat and oxygen from the fuel source, extinguishing the fire. The effectiveness of the intumescent flame retardant such as silicate is its ability to form a char on the surface of the burning material. The char acts as a physical barrier against heat transfer to the surface of the combustible material. Char formation lowers the rate of temperature increase of the surface beneath the char.

5.4 Thermal Stability of PLA/Natural Fiber Composites

Thermal stability of PLA and its composites have been reported in the literature [12]. Thermal decomposition of PLA depends on the sample preparation in which some authors reported one degradation step corresponding to thermal decomposition of PLA [55, 82]. Other reported two degradation steps: (i) evaporation of water adsorbed to the samples which are usually below 100 °C and (ii) between 280 to 400 °C corresponds to PLA degradation. The decomposition of PLA involves simultaneous reactions with the main products being carbon dioxide, acetaldehyde, carbon monoxide, ketone, lactide, and cyclic oligomers [35, 36, 82]. DTG curve is often broad correlating to those various reactions and the resulting products. Various mechanisms have been proposed to explain thermal decomposition of PLA which include non-radical and radical reactions: random chain scission reactions, depolymerization, oxidative degradation, intramolecular and intermolecular transesterifications, hydrolysis, pyrolytic elimination, and radical reactions [12]. Carrasco et al. [12] studied the influence of processing method (injection and extrusion/injection) as well as annealing of PLA on the thermal stability of the resulting material. The authors compared unprocessed raw PLA (PLA-V), injected PLA (PLA-I), extruded and injected (PLA-EI), injected and annealed (PLA-IA), as well as extruded, injected, and annealed (PLA-EIA). Raw material (PLA-V) had slightly higher thermal stability compared to that of processed and annealed materials. By comparison of the degradation temperature at 5 (T_5), 50 (T_{50}), and 95% (T_{95}) weight loss as well as maximum thermal degradation peak (T_p), it was reported that the raw material had higher thermal stability compared to all processed materials due to chain scissions during processing, resulting in shorter and higher number of short chains. A linear relationship between the thermal stability (T_5) and average molecular weight was also obtained. The higher molecular weight samples led to more thermally stable materials due to the presence of shorter chains in the case samples having low molecular weight. As expected, the materials with higher polydispersity index led to low thermal stability since a material with high polydispersity contains small molecules which are more volatile. It was concluded that during thermal processing, PLA degrades to a certain extent (i.e., depending on the processing conditions) giving rise to MFI values with a decrease in viscosity (due to a decrease in molecular weight) which decrease thermal stability of PLA. Therefore, it is of significance to choose suitable processing conditions to overcome the degradation of PLA during processing. It is worth mentioning that the processing conditions used did not modify the chemical composition of PLA. Cross-linking of neat PLA can also be used to enhance the thermal stability of PLA as reported by Wu et al. [80].

The addition of natural fibers having lower thermal stability as compared to neat PLA reduces the thermal stability of the resulting composite product [55, 74, 87, 89]. As expected, thermal stability also decreases with an increase in low thermally stable natural fiber content since these fillers accelerate the thermal decomposition of PLA [55, 74]. The hydrophilic property of natural fibers promotes weak adhesion of water onto the PLA/natural fiber composites which are usually reflected in the mass

loss (5–10%) at temperatures below 100 °C. The second step occurs between 300 and 370 °C with the last third step above 370 °C related to complete degradation of the composite material. It is recognized that the presence of moisture (which causes hydrolysis), lactic acid residues, and metal catalysts facilitates the PLA degradation [12, 89]. The hydrophilic property of natural fibers led to water absorption by composite products which in turn promotes PLA thermal degradation via hydrolytic scission [89]. Zhang et al. [89] studied the thermal properties of PLA with three kinds of fibers, i.e., bamboo fibers, wood fibers, and coconut fibers. They found that the composites (i.e., regardless of fiber kind) degraded through three steps: (i) the dehydration of weakly bound moisture during storage nearly at 100 °C with a mass loss of 10%; (ii) a second step occurred from 300 to 370 °C corresponding to thermal degradation of natural fibers; and (iii) after 370 °C, the composites started to thermal decompose. The opposite behavior was reported by Yusuf et al. [87]. It was stated that the composition of the fibers can influence the thermal stability of the resulting composite product. It was found that at a weight loss of 10%, PLA/rice husk composites degrade at 305 °C, while PLA/kenaf degraded at 321 °C. In the case of 75% weight loss, PLA/kenaf degraded at 357 °C and PLA/rice husk at 340 °C. This was attributed to the difference in chemical composition of these fibers. Kenaf fiber has a low content of lignin with a high content of cellulose which is more thermally stable. With regard to the fiber composition, their treatment before adding into the PLA matrix could affect the thermal stability of the ensuing polymer composites [21]. These treatments are often employed to remove some of the components of the fibers to improve the interfacial adhesion between the filler and the polymeric matrix. Modification of the fibers with hydrogen peroxide and sodium hydroxide, followed by the extrusion with PLA as the matrix, was reported by Sun et al. [74]. They found that the thermal stability of the composite material decreased with an increase in modified fiber content due to the low thermal stability of the fibers compared to neat polymer. Similar observations were reported in Gunti et al. [21]. The authors used both peroxide and sodium hydroxide to treat the fibers.

Flame retardants are often added to flammable materials to reduce the impact of fire on people, property, and the environment. Since natural fibers are flammable, there has been growing interest in treating them with flame retardants to widen their application of advanced composite materials. The addition and/or treatment of natural fibers with flame retardants not only were found improving the flammability resistance of the composite materials but also enhanced their overall thermal stability [71, 72, 84, 83]. Suardana et al. [72] reported that the treatment of the fibers with diammonium phosphate (DAP) reduced the decomposition rate of PLA composites and increased the residual char. This was attributed to the presence of lignin which acts as a source of carbon during thermal degradation of the natural fibers [72]. On the other hand, Shukor et al. [71] investigated the treatment of the fibers with NaOH, followed by the addition of ammonium phosphate (DAP). It was reported that the addition of only 15% of ammonium phosphate into untreated fibers resulted in no influence on the thermal stability of neat PLA, while the NaOH-treated fibers improved the thermal stability of the resulting composite material but decreased residual char residue. The latter was ascribed to the NaOH treatment which removes lignin

(which is a source of carbon during degradation) from the fibers. It was demonstrated that the incorporation of the flame retardants compromises the interaction between the fibers and PLA and hence compromises the resulting mechanical properties. The optimal content of the flame retardants is often required in order to get the balance between the thermal stability and mechanical properties.

Coupling agents/compatibilizers are usually employed to facilitate the interaction as well as the dispersion of the fibers in PLA host matrix [26, 66, 85, 90]. In general, the composites in which compatibilizers were utilized showed higher thermal stability when compared to the un-compatibilized system. This has been associated with two factors: (i) the strong interaction between the fiber and PLA (in which the degradation of fibers due to their low thermal stability acts as insulating layer to protect PLA or traps volatile products and delays their diffusion) and (ii) the increase in molecular weight by cross-linking of PLA and the fibers or molecular chain extension. Table 9 summarizes selected studies based on PLA/natural fiber-reinforced composites.

6 Conclusion

The development of composites from biodegradable polymers and natural fibers has attracted the attention of scientists because of increasing environmental concerns. Natural fibers as reinforcing could significantly lower the price of bio-based composites which is still a problem for extensive applications of these materials. Because they are also obtained from renewable resources, they can replace conventional fillers such as glass, carbon, and Kevlar. Furthermore, natural fibers possess reduced tool wear and enhanced energy recovery and can also improve the mechanical properties of biopolymer matrices. Generally, it has been reported that the tensile and flexural moduli of PLA matrix are improved with the addition of natural fibers, with the properties improving further for treated fiber biocomposites. A PLA/natural fiber composite has some limitations which impede its success in various applications such as poor flammability resistance and high moisture absorption. The enhancement in flammability resistance of PLA/natural fiber biocomposites was done by chemical treatment of fiber with flame retardants' chemical compounds (e.g., diammonium phosphate (DAP). The disadvantages (viz, high flammability, low tensile properties, and high moisture absorption) that the biocomposite made of PLA/natural fiber possesses were mostly addressed by researchers through different chemical treatments. The higher commercial prices of biodegradable polymers in comparison with commercially available petroleum-based polymers can be counter balanced by their lower disposal costs which should be taken into account in the future. One could still expect that the price of biodegradable polymers, especially those produced from natural sources to decrease in the coming years to ensure that biodegradable polymers, can replace traditional polymers. This can simply solve a huge problem that we are currently facing with regard to waste disposal of traditional polymer-based materials.

Table 9 Summary of selected studies based on the thermal stability of PLA/natural fiber composites

Sample	Treatment of fiber	Comments	References
PLA/rice husk and PLA/kenaf fiber	–	All composites showed inferior thermal stability as compared to neat PLA, but PLA/kenaf composites displayed superior thermal stability when compared to the rice husk-based composites due to the composition of the fibers (kenaf has high cellulose content which is thermally stable)	Yussuf et al. [87]
PLA/ramie	Sodium hydroxide (NaOH) followed by silane (3-aminopropyltriethoxysilane and γ-glycidoxypropyltrimethoxysilane)	The composites of untreated fibers showed lower thermal degradation temperature than that of neat PLA due to a decrease in molecular weight of PLA from the thermal processing, whereas chemically treated fibers improved the thermal stability of PLA which was attributed to the strong interaction between PLA and fibers	Yu et al. [85]
PLA/rice straw fiber (RSF)	Methyl methacrylate (MMA) was employed as a monomer in admicellar polymerization for RSF treatment	The treatment enhanced thermal stability on the composites as compared to neat PLA as well as untreated fiber composites	Zhao et al. [90]
PLA/RSF	Suspension polymerization of butyl acrylate (BA) as fiber treatment	Thermal stability increased with increase in butyl acrylate content	Qin et al. [61]
PLA/kenaf fiber	NaOH followed by thymol	There was no significant influence on the thermal degradation behavior of PLA	Tawakkal et al. [76]
PLA/banana fiber	NaOH and silane (3-aminopropyltriethoxysilane (APS) bis-(3-triethoxy silyl propyl) sulfate (Si69)	All composites for treated composites showed higher thermal stability, but Si69 displayed superior thermal stability compared to all other composites. This was attributed to cross-linking and chain extension of PLA	Jandas et al. [26]

The future is promising for green biocomposites in order to produce advanced composite materials.

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Chapter 3
Opportunities for PLA and Its Blends in Various Applications

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1 Introduction

Biopolymers derived from renewable resources garnered much attention due to increasing environmental concerns and the volatility of oil prices with regard to our dependence on petroleum-based polymers [7, 33, 53, 94]. Polylactic acid (PLA), also known as polylactide, merits special interest owing to its unique properties such as excellent biodegradability, biocompatibility, good mechanical strength and easy processability. It was first introduced into the market in the early 1880s [94] and its monomer, lactic acid (2-hydroxy propionic acid), was first isolated from sour milk by Scheele in 1780. PLA is now commercially produced by fermentation of renewable

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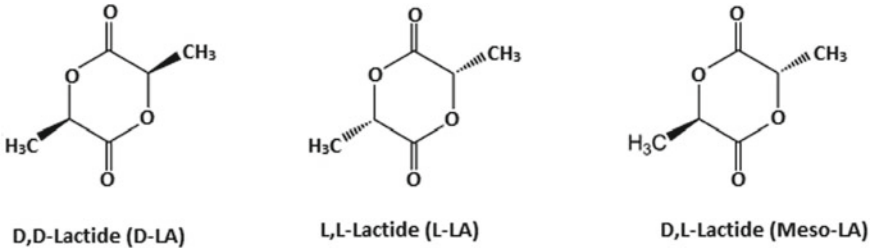

Fig. 1 Chemical structure of Lactide stereoisomers

resources such as corn, starch, sugar beet and other agricultural-based waste materials to lactic acid. The most common route to produced PLA is by ring-opening polymerization (ROP) of lactide in the presence of a metal catalyst, usually tin octoate [7, 33, 53, 94]. Lactide is a dimer which is often prepared by depolymerization of low molecular weight PLA oligomer. Besides ROP, other techniques were utilized to produce high molecular weight PLA such as chain extension reaction, azeotropic dehydration condensation and melt/solid state polymerization [25, 39, 46].

The presence of two chiral carbon centers results in lactide having three stereoisomers, i.e., D, D-lactide, L, L-lactide and D, L-lactide as shown in Fig. 1. The stereochemical composition plays a major role on the physical properties viz. melting temperature, crystallization behavior and mechanical properties of PLA [7, 33, 53, 94]. For example, a mixture of 1:1 ratio of poly(D-lactide) and poly(D-lactide) results in high melting temperature (~230 °C) and good mechanical properties when compared to PLA homo-polymers polymerized from pure poly(L-lactide) and poly(D-lactide) [94]. Therefore, the three available PLA are poly(L-lactide), poly(D-lactide) and poly(D,L-lactide). The commercially available PLA is a copolymer composed of poly(L-lactide) and a small amount of poly(D-lactide) since it is produced from natural resources.

As mentioned earlier in this document, PLA is derived from renewable resources (corn, starch, sugar beet and other agricultural-based waste); hence it is relatively cheaper, recyclable, compostable and biodegradable [7, 33, 39, 53]. It is easily processable using conventional equipment with good biocompatibility and bioresorbability. Moreover, it has high tensile modulus (1.7–3.5 GPa) and tensile strength (50–70 MPa) [7, 33, 39, 53]. Owing to its unique properties, PLA has to potential to replace petroleum-based plastics in various fields such as biomedical, pharmaceuticals and packaging.

Despite these attractive advantages and its capability to replace petroleum-based polymers in certain fields, it has some drawbacks that limit its application. It is brittle and has low impact resistance which limits its application where good impact resistance is required [42, 94]. Furthermore, PLA has poor crystallization and slow biodegradation rate which also constricts its application. There has been much interest from industrial and academic communities to overcome these limitations in order to improve PLA performance in various fields. Different modifications such as copoly-

merization and blending with other biopolymers have been researched as discussed in this chapter. Other strategies to improve the compatibility between PLA and other biopolymers are the addition of nanofillers and third polymer as highlighted in this chapter.

2 PLA Modifications

In order to further extend the application of PLA in various fields, a wide variety of techniques are used for its modification, namely incorporation of fillers and reinforcements, plasticization, blending and copolymerization. With these techniques, it is possible to adjust the properties of PLA for the intended application, especially its ductility. These techniques have advantages and some drawbacks as it will be discussed in this chapter.

2.1 Chemical Polymerization

Copolymerization provides with the opportunity to synthesize novel materials with various properties. A wide variety of polymers viz. polyesters, polyolefin and natural have been copolymerized with PLA to overcome its limitations for different applications as reviewed by Hu et al. [39]. The presence of carboxyl and hydroxyl groups on Lactic acid renders an option for copolymerization with other monomers. The copolymerization processes techniques such as condensation polymerization [63, 93], ROP [27] and chain extension reaction [27, 95] were reported in the literature for modification of PLA properties. Feng et al. [29] studied the modification of PLA using chain extension or transesterification. In this study, the poly(ether urethanes)s (PEUs) with different molecular weight were synthesized to evaluate the effect of molecular weight and content of PEUs on tensile properties of the blends. Triphenyl phosphite (TPP) was used as a transesterification catalyst or coupling agent. It was reported that without TPP, the elongation at break of the blends with 5–30wt% PEUs was less than 30%, however, in the presence of TPP, the values were above 240% due to intermolecular reactions between PLA and PEU with the addition of TPP, regardless of PEUs molecular weight. It is worth mentioning that the tensile strength and modulus decreased with increase in PEUs content. In the follow-up study [30], the authors used a polyurethane based on poly(ethylene glycol)-b-polylactide copolymers (PELU) prepared by chain extension with isophorone diisocyanate (IPDI). At PELU content of 5–20 wt%, the blends with PLA segment content of 5, 10, 20 and 30% displayed two-phase sea-island structure with PELU dispersed in the continuous PLA phase, and there was the obvious interface between these phases as shown in Fig. 2. It was found that the dispersed phase increased with increase in PELU content and decreased with increasing PLA segment. The blends with PLA segment content of 40 and 50 exhibited a homogeneous phase, and there was no interface

between PLA and PELU signifying compatibility (Fig. 2). In case of mechanical properties, at PELU content of 10–20 wt% the elongation at break ranged between 250 and 350% for blends with PLA segment of 40 and 50%, respectively, whereas at 20 wt% PELU the tensile strength and modulus for PLA segment content 30–50 reached a value of 35–38 MPa and 1300–1500 MPa. One could realize that copolymerization offers an advantage with regard to the availability of different polymers that can be selected to modify PLA to afford various properties. Furthermore, copolymerization is important in controllability of the structural architecture and molecular weight which directly depend on the molecular composition of the copolymer. It can be argued that copolymerization often results in the improvement of polymer properties by compromising other properties. It was realized that copolymerization of PLA/PCL system by ROP reached elongation at break values above 600%, while tensile strength and modulus decreased to 32 and 30 MPa, respectively [27]. On the other hand, the chemical polymerization processes involve complex controlled conditions, long periods of time and it is costly. For instance, Pivsa-Art et al. [63] copolymerized L-lactide acid (LLA) and E-caprolactam using two different procedures. The first procedure involved copolyester-amide prepared via oligomers of L-lactide acid (OLLA) and ε-caprolactam ratio 50:50 by weight using tin (II) chloride as catalyst at 120 and 180 °C for 5 h under atmospheric pressure, whereas the second procedure was carried out using OLLA and ε-caprolactam ratios 90:10, 80:20, 70:30, 60:40 and 50:50 at 130, 150 and 180 °C under 30 Torr for 3 h. It was found that the products from the first procedure were a yellowish paste and brown viscous for respective 120 and 180 °C, which could not be analyzed further. In the second process at 150 and 170 °C, it was possible to produce copolyester-amides having higher crystallinity and the melting temperature which was found to increase with an increase of ε-caprolactam content, but decreased when the amount exceeds 30%.

2.2 Blending

2.2.1 Plasticizers

The theory behind plasticization involves the exchange of intermolecular bonds among polymer chains such that there are bonds between the macromolecules and low molecular weight compound which promote conformational changes resulting in deformability. This decreases the glass transition and melting temperatures, hence processing temperature of the resulting material. In the case of PLA, the addition of plasticizer does not affect only the abovementioned properties, but the overall mechanical properties. Different compounds have been utilized as a plasticizer to modify PLA especially to improve its ductility. This includes glycerol [48], polyethylene glycol [36], oligomeric lactic acid [48] and different esters [37, 44]. In general, the concentration of these plasticizers ranges between 10 and 30 wt%. High concentrations of plasticizers were utilized by Li and Huneault [47] for thermoplastic starch (TSP)/PLA blends. The concentration of plasticizers was varied between 30 and 42%,

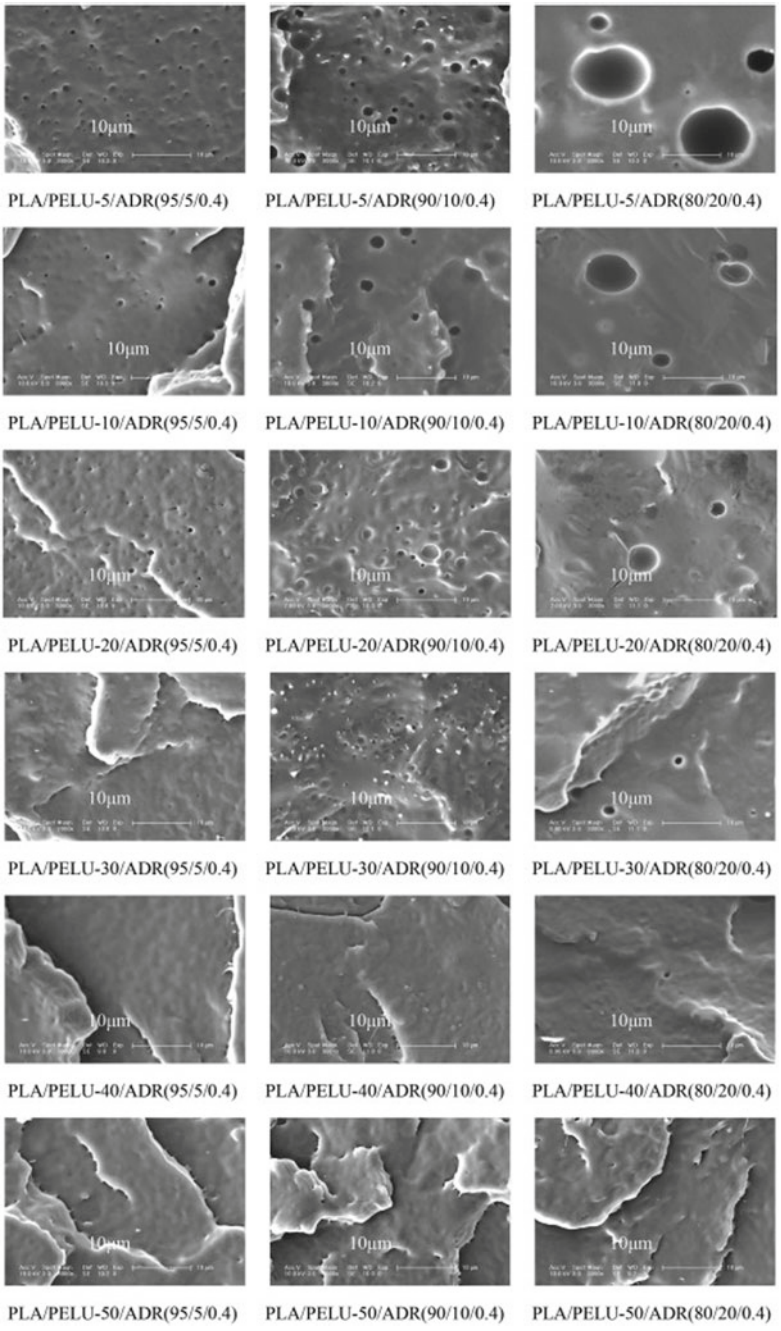

Fig. 2 SEM micrographs of cryo-fracture surfaces of PLA/PELU blends [30]

while TPS content was varied from 27 to 60% on a weight basis. It was reported that the ratio of glycerol/sorbitol plays major on the properties of the ensuing blends. However, finer morphologies and good tensile properties were found for the sorbitol plasticized blends. On the other hand, low molecular weight compounds have been studied as potential plasticizers of PLA, namely D-limonene [5], carvacrol [3] and thymol [67, 77]. It is worth noting that most of the plasticizers used for PLA are often adapted in its blends to further improve its toughness. Fortunita et al. [33] investigated the effect of two plasticizers, i.e., acetyl tributyl citrate (ATBC) and isosorbide diester (ISE) on PLA/PBS blend for film stretchability. It was found that 15 wt% of ISE was the best choice to plasticize the blend. The use of renewable-based plasticizers received much attention as replacement of petroleum-based plasticizers. The addition of polyester plasticizer (Lapol 108, Mw = 80 000 g mol^{-1}) derived from more than 50% renewable resources into PLA/PHB blend was studied by Abdelwahab et al. [1]. The glass transition temperature of PLA decreased from 62 °C in PLA/PHB blend to 58 °C with only 7 wt% of Lapol 108, while elongation increased from 7 to 15%. Most of these plasticizers have a low molecular weight which leads to their evaporation especially when processing with techniques where heat is involved [6]. Arrieta et al. [6] reported that about 30% of limonene was evaporated during processing of the blend though the loss was less for 15 wt% of limonene when compared to PLA-limonene system in which 40 wt% was lost during processing. Similar behavior was reported by Armentano et al. [3] in which a 25% loss of carvacrol as a plasticizer for PLA/PHB blend during processing was obtained. Ferri et al. [32] investigated the potential of maleinized linseed oil (MLO) as a plasticizer and reported a decrease in the glass transition temperature by 6.5 °C when compared to neat PLA. They observed plastic deformation with a maximum elongation of 5 phr MLO, however, phase separation was observed at higher MLO content (15–20 phr) which had a negative effect on the overall toughness. Carbonell-Verdu et al. [21] assessed the potential of maleinized cottonseed oil (MCSO) as a plasticizer of PLA films. The addition of MCSO slightly decreased T_g of neat PLA from 63 to 60–61 °C. A maximum elongation at break of 292% was achieved by the addition of 7 wt% of MCSO. However, the overall disintegration of the PLA formulations was not influenced by the presence of MSCO, therefore, MCSO can be used as an environmentally friendly additive to enhance the ductility of PLA-based films. Carbonell-Verdu et al. [21] reported that a balance between the ductility and mechanical resistance can be obtained by using maleinized hemp seed oil (MHO) as plasticizer for PLA because of simultaneous linear chain extension, branching, and/or cross-linking phenomena resulting from the reaction of the multiple maleic anhydride (MAH) groups present in MHO with the terminal hydroxyl groups of the PLA chains.

2.2.2 PLA/Biodegradable Polymers

Polymer blending is one of the most feasible cost-effective methods to produce a new material when compared to chemical copolymerization. In the past years, research has escalated in blending PLA with other suitable polymers which have good

flexibility, excellent impact strength and melt processability to modify its properties and lowers the cost [49, 62, 66]. It is worth mentioning that only biopolymers will be overviewed in this chapter. Despite the fact that the addition of the non-biodegradable polymers renders an advantage to modify PLA, the natural-based polymers received more interest because they offer property improvements without compromising the biodegradability. However, the miscibility between PLA and other biopolymers is influenced by certain factors such as processing temperature, the proportion of each component in the blend and their molecular weight. For instance, several authors blended PLA with PBS because of its ductility and high impact strength as well as thermal and chemical stability [33]. In these studies, it was found that 20 wt% is the maximum PBS content to afford miscibility with PLA. It was also reported that PBS decreased tensile strength and modulus, while elongation at break increased with PBS content.

PLA/Thermoplastic starch: Numerous studies were reported on blending thermoplastic starch (TPS) and PLA, especially for packaging [13, 53, 73, 85]. In most cases, a plasticizer for starch is often included in the system to improve its processability. Among all plasticizers, glycerol is the most used. The flexibility of TPS depends on the moisture and/or glycerol content as well as its source [13, 73, 85]. It has a tensile strength ranging between 0.4 and 38 MPa, and elongation at break value can reach 129%, depending on moisture content or other components, such as glycerol. A combination of brittle PLA and flexible TPS can lead to a mechanically balanced product that can be applied in various applications, especially in packaging. Solution casting and melt compounding are the most used processing techniques to produce PLA/TPS blend materials. Le Bolay et al. [45] avoided both plasticizer and compatibilizer for PLA-TPS blend by using the co-grinding method. Optimization of operating conditions improved the dispersion of the starch filler in the PLA matrix without compatibilizer or plasticizer which offers production of composite material with good use properties.

PLA/Natural rubber (NR): Natural rubber (NR) is one of the vital agricultural products which is used in the manufacture of various consumer products. This is because of its valuable properties such as high strength (tensile and tear) and excellent elasticity. The use of natural rubber as a modifier for PLA has been reported by numerous authors [24, 41, 69, 74, 88, 91, 92]. The main aim was to exploit the flexibility of natural rubber in which the rubber particles behave like stress concentrators enhancing the fracture energy absorption of brittle PLA and yielding toughened material. Some petroleum-based elastomers such as thermoplastic polyurethane(TPU) [35, 90], polyurethane [11, 40], poly(ethylene-glycidyl methacrylate) (EGMA) [59] and polyamide elastomer (PAE) [98] were also blended with PLA to improve its toughness. In all these studies, ductility of PLA was enhanced, however, these synthetic rubbers are mostly from petroleum-based materials which are not good from an environmental viewpoint. Therefore, natural rubber as an agricultural product from renewable material features unique properties such as biocompatibility and biodegradability which makes it ideal candidates in order to improve the toughness of PLA. A number of studies based on PLA/NR reported that optimal content of NR is 10 wt% to obtain maximum impact strength [14–16, 41]. The processor can

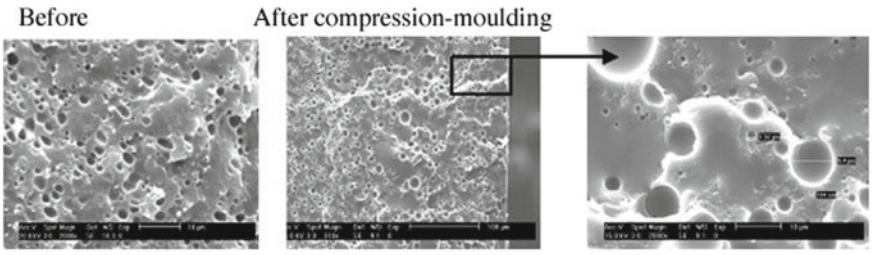

Fig. 3 Comparison of PLA/NR 20 wt% blend morphology before and after compression molding [15]

play around with the processing parameters (temperature, time and rotor rate) in order to control the size and the dispersion of the rubber particles in the host matrix which in turn influences the properties of the resulting blends. Bitinis et al. [15] prepared PLA/NR blend at varying temperature (160, 180 and 200 °C) while rotor rate and blending time were fixed at 60 rpm and 15 min, respectively. Besides the phase separation exhibited by the blends, the NR average droplet size increased with temperature and their dispersion became broader. In case of varying the rotor speed (30, 60 and 90 rpm) and time (10 and 15 min) keeping other variables constant, it was found that the morphology was hardly influenced. Interestingly, the elongation at break increased from 5 to 200% with the addition of only 10 wt% of natural rubber without a compatibilizer. However, at higher content, 20 wt% of NR the coalescence of NR droplets during compression molding led to infective toughening of PLA (Fig. 3). It was reported that the extent of this phenomenon in the case of 10 and 5 wt% of NR was less pronounced thus did not affect their mechanical properties. Xu et al. [88] also reported that the difference in melt viscosity between PLA and NR resulted in coalescence at higher concentration of NR which led to an ineffective toughening of PLA. Nevertheless, authors reported that NR phase at 35 wt% NR had a network-like structure which led to high impact strength (500 J/m), i.e., 7 times that of neat PLA.

PLA/Poly(hydroxyalkanoates) (PHAs): PHAs are family of biologically synthesized biopolymers by controlled bacterial fermentation [52, 68]. They are biopolyesters of hydroxyalkanoates (HAs) synthesized by numerous bacteria as carbon and energy storage compounds. PHAs are semi-crystalline high molecular weight polymers. Most of the polymers from this family have low thermal resistance with narrow processing temperature close to their thermal degradation. The application of these polymers in various fields is restricted by their brittleness and expensiveness. Blending PLA with PHAs is another suitable solution to overcome some of its limitations. The most studied biopolymer from PHAs family is poly(hydroxybutyrate) (PHB) owing to its properties comparable to most synthetic polymers. The blends of PLA and PHB were reported to be immiscible despite their relatively low solubility difference (solubility parameter for PLA and PHB is 19.5–20.5 $MPa^{1/2}$ and 18.5–20.1 $MPa^{1/2}$, respectively). Their miscibility

was found to be directly depended on the processing technique, molecular weight and the proportion of each component. Ohkoshi et al. [56] investigated the effect of molecular weight on PLA/PHB blend by blending high molecular weight PLA (778,000 g mol^{-1}) with different molecular weight PHB (viz. 9400, 21,000 and 140,000 g mol^{-1}) through solution casting and further melt processed by compression molding. They stated that melt-compressed samples of PLA and PHB with low molecular weight (9400 g mol^{-1}) were miscible up to 50 wt% of PHB because the addition of PHB facilitated the crystallization of PLA. Both high molecular weight PLA and PHB were immiscible, however low molecular PLA was miscible in the melt over the whole composition range [17]. PHB addition into PLA often increases Young's modulus, while tensile strength and elongation at break decrease with an increase in PHB content [3, 4, 7, 96]. It is worth mentioning that all these properties depend mostly on the proportion of the blend component. A high proportion of PHB blend (up to 60 wt%) results in a brittle material with fairly low elongation at break (i.e., below 3%), while below 40 wt% PHB the resulting blend material behaves like classic thermoplastic polymer.

PLA/polycaprolactone (PCL): Numerous researchers reported on the blends of polycaprolactone (PCL) and PLA [22, 50, 60, 82]. PCL is a more flexible biopolymer with low melting (~60 °C) and glass transition temperature (~−60 °C). PCL/PLA blends have a promising potential in different applications such as tissue engineering [61], drug release [20], bone fixation devices [76] and food packaging [19]. In general, the flexibility/ductility of PCL plays an important role in the resulting mechanical properties of the blends. It was found that the presence of PCL increased the impact strength and elongation at break when compared to PLA [58, 78]. However, the tensile strength and modulus were compromised by the addition of PCL. Phase separation is usually obtained due to immiscibility between these components with PCL particles/droplets size increasing with PCL content in PLA. [78] studied the effect of processing method (viz. injection molding and hot pressing) on the resulting properties of the PCL/PLA blend. It was found that all the blends were immiscible. It was reported that the injection molded specimens showed ductile behavior with elongation reaching values close to 140%, while melt pressed ones reached ~50% due to the difference in PCL size in PLA. The melt pressed samples exhibited larger particle size as compared to injection molded samples. The impact strength was found to increase with an increase in PCL content with ~200% with 30 wt% and 350% with 40 wt% PCL. The optimization of composition and processing of PLA/PCL blends were conducted by Ostafinska et al. [58]. In this study, PLA and PCL were chosen such that the viscosity ratio is approximately 1 and the sample composition was varied from 15 to 50 wt% of PCL in PLA. At low PCL content, i.e., below 25 wt%, the blends showed a fine phase structure with small particles and narrow particle size distribution, whereas at 30 wt% the phase structure became coarser with broader particle distribution. A co-continuous structure was observed at high PCL content viz. above 40 wt%. The impact strength of the blends increased with PCL content reaching maximum at 20 wt%. This composition (80/20 PLA/PCL) exhibited high impact strength exceeding pure PCL and 16 times higher than PLA. This was attributed to the particle size of the PCL in PLA at this composition and

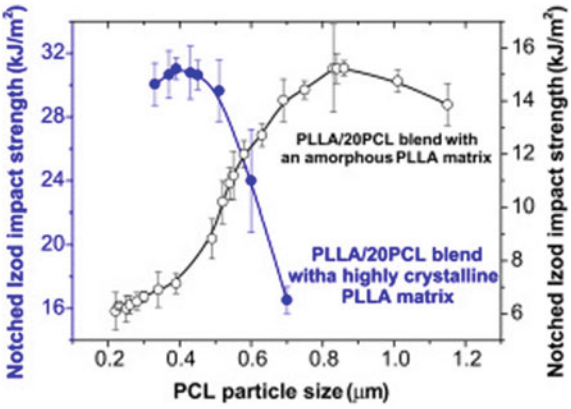

Fig. 4 Comparison of the difference in optimum particle size for toughening PLA/20PCL blend with an amorphous PLA matrix and for that with a highly crystalline PLA matrix [9]

a synergistic effect from the blends' components. In most cases, the properties of each polymer (PLA and PCL) such as crystallinity play a major role in the size of the particles in the resulting blend. This, in turn, influences the impact properties of the blend as reported by Bai et al. [9]. The optimum particle size ranged between 0.3 and 0.5 μm for crystalline PLA and 0.7–1.1 μm for amorphous PLA (Fig. 4). The difference between these cases was related to the synergistic effect of PLA matrix crystallization and PCL particle size contributing to toughening and desirable toughening efficiency.

PLA/poly(butylene adipate-co-terephthalate) PBAT: PLA/PBAT blends were investigated by a number of researchers due to the high flexibility and biodegradability of PBAT [38, 70, 72, 83, 84]. PBAT is an aliphatic-aromatic polyester having carbonyl groups along polymer chain which is usually exploited for compatibility with PLA. It is a random copolymer composed of butylene adipate and terephthalate prepared by melt polycondensation of 1,4-butanediol, dimethyl terephthalate and adipic acid and catalyzed by tetrabutylorthotitanate. The butylene adipate group is responsible for its biodegradation, while the terephthalate group contributes toward its stability and mechanical properties with an elongation at break reaching 700% and tensile strength of 32 MPa. Its high-cost production relies on petroleum resources as raw materials which hinders its success in various applications. Thus blending with biodegradable such as PLA is of significance not only to improve the mechanical properties of the resulting blend but to reduce the overall cost of the final product. The immiscibility between PLA and PBAT is recognized by phase separated morphology, especially at a concentration higher than 5 wt% [26, 89]. Yeh et al. [89] reported that PLA and PBAT are compatible with a concentration of 2.5 wt% and below. The authors reported that the elongation at break increased with an increase in PBAT content at the expense of tensile strength.

Although blending PLA with other biopolymers sounds straightforward, there are some concerns to produce a blend with high performance because of limited and/or no stress transfer between the blend components. Thus, there has been much

interest to improve the interfacial adhesion between the PLA blends' components as discussed in the next section.

3 Compatibilization Strategies

Compatibilization is a process in which the compatibility of the two polymers can be enhanced in order to improve the resulting properties. As mentioned earlier in this document that PLA is immiscible with most of the available polymers, thus the resulting blends tend to be useless unless compatibilized. It is of significance to define some important terms when it comes to miscibility of polymer blends before we discuss in detail the compatibilization strategies. In general, the miscibility of polymers can be classified into three: completely miscible, partially miscible and immiscible. Completely miscible polymer blends feature homogeneous morphology (one phase) with one glass transition temperature (T_g), while partially miscible exhibit two phases morphology with some part of the one polymer dissolved in the other. In this case, two T_g representing both polymers are obtained with one T_g shifting toward the T_g of the other polymer component. However, for the immiscible blend, macro-separated morphology with the course interface is observed with two distinctive T_g for both polymers in the system. Therefore, compatibilization is of significant importance to change the course interface to a fine one in order to enhance the blend performance or to obtain the contribution of both blend components on the resulting properties.

3.1 Chemical

Copolymers having functional groups compatible with PLA and the second polymer usually situate at the interface to enhance interfacial adhesion [22, 82]. Chavalitpanya and Phattanarudee [22] studied compatibilization of PLA/PCL blends using a block copolymer of poly(ethylene glycol) and poly(propylene glycol) (PEG-PPG). The blend ratio was kept at 80/20 while the copolymer was varied from 0 to 10 phr. The increase in PEG-PPG content resulted in an increase in strain at break, and at the same time, tensile stress and modulus decreased. The optimal concentration of copolymer was 7.5 phr at which strain at break reached 74%, i.e., 10 times than that of neat PLA/PCL blend. The improvement of the mechanical properties was attributed to the PEG block copolymer being compatible with PLA, therefore generating a strong interfacial adhesion between the components. Wachirahuttapong et al. [82] used poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) (PEG-PPG-PEG) copolymer and found that the ductility of the blend was increased by the presence of copolymer. In a study Shin et al. [71], chemically modified thermoplastic starch (CMPS) was blended with PLA using twin screw extruder. Although the blends were thermodynamically immiscible, the interfacial adhesion was improved by the PLA-g-starch copolymers that were formed at the interface through a transesterifica-

tion reaction. However, the tensile strength and elongation decreased gradually with an increase in CMPS content due to lack of stress transfer between the phases.

Poly(glycerol succinate-co-maleate) is composed of three monomers, i.e., maleic anhydride, glycerol and succinic acid [79, 80, 81]. Interestingly, glycerol and succinic acid are biobased, whereas maleic anhydride is from synthetic routes [80]. The presence of these functional groups is found to promote interfacial adhesion by reacting with the biopolymer terminal groups. Valerio et al. [80] fabricated PLA/poly(glycerol succinate-co-maleate) (PGSMA) blend using dynamic vulcanization strategy involving simultaneous cross-linking and compatibilization of PGSMA within the PLA matrix on reactive extrusion. During melt compounding of PLA and PGSMA in the presence a free radical initiator results in different reaction products (Fig. 5), and the free radical attacks C = C double bond on PGSMA molecules creating macroradicals. These radicals can react with themselves (I Fig. 5) or promote hydrogen abstraction from PLA backbone which could attack by PGSMA macroradicals to yield grafting of PGSMA molecules onto PLA backbone to form PLA-g-PGSMA copolymers (II Fig. 5). The other possibility is transesterification between ester groups on PLA and PGSMA and/or the esterification reaction between OH and COOH end groups of PLA or PGSMA (III Fig. 5). In order to maximize toughness of the blend, the low transition temperature of −1.69 °C was found by setting the succinic acid to maleic anhydride content of the PGSMA synthesis to 1:0.75:0.25 mol glycerol: succinic acid: maleic anhydride, yielding a C = C bearing PGSMA. It was reported that interfacial adhesion (B) of the blend reached the value of 0.744 according to the Pukanzky model owing to the formation of PLA-g-PGSMA copolymers. The blends containing 60/40 wt% of PLA/PGSMA displayed an increment in their elongation at break and impact resistance of 53 and 175% when compared to neat PLA.

Reactive polymers with epoxy groups were also studied with the aim of improving the interfacial adhesion between PLA and other biopolymers [8]. In order to improve the mechanical properties of immiscible PLA/PBAT blends, Arruda et al. [8] compatibilized the blends with commercially available multifunctional epoxide (Joncryl ADR 4368) containing epoxy with equivalent weight of 285 g/mol and found that the presence of the chain extender improved the ductility of the blend. The soybean derivatives such as epoxidized soybean (ESO), maleinized soybean oil (MSO) and acrylated epoxidized soybean oil (AESO) were utilized to compatibilizer a ternary blends of PLA, PCL and PHB (with a constant weight percentage of 60, 10 and 30%, respectively) [34]. The presence of functionalities, i.e., epoxy, acrylic acid and maleic anhydride in ESO, AESO and MSO, respectively, offers an opportunity to react with the terminal hydroxyl groups of all three polyesters which result in compatibilization effect as shown in Fig. 6. PLA with its brittle nature displayed elongation at break of 7.87% and high tensile modulus and strength of 3.6 GPa and 58.2 MPa, respectively. In the case of a ternary blend, elongation at break reached 15.3% and tensile modulus and strength decreased to 2 GPa and 48.4 MPa, respectively, because of the ductility of PCL component. In comparison with conventional compatibilizer ESAO, the compatibilization of PLA/PCL/PHB with AESO gave similar results with an elongation at break reaching 45% as well as tensile modulus and strength values of 43–44 MPa and 1.8–1.9 GPa, respectively.

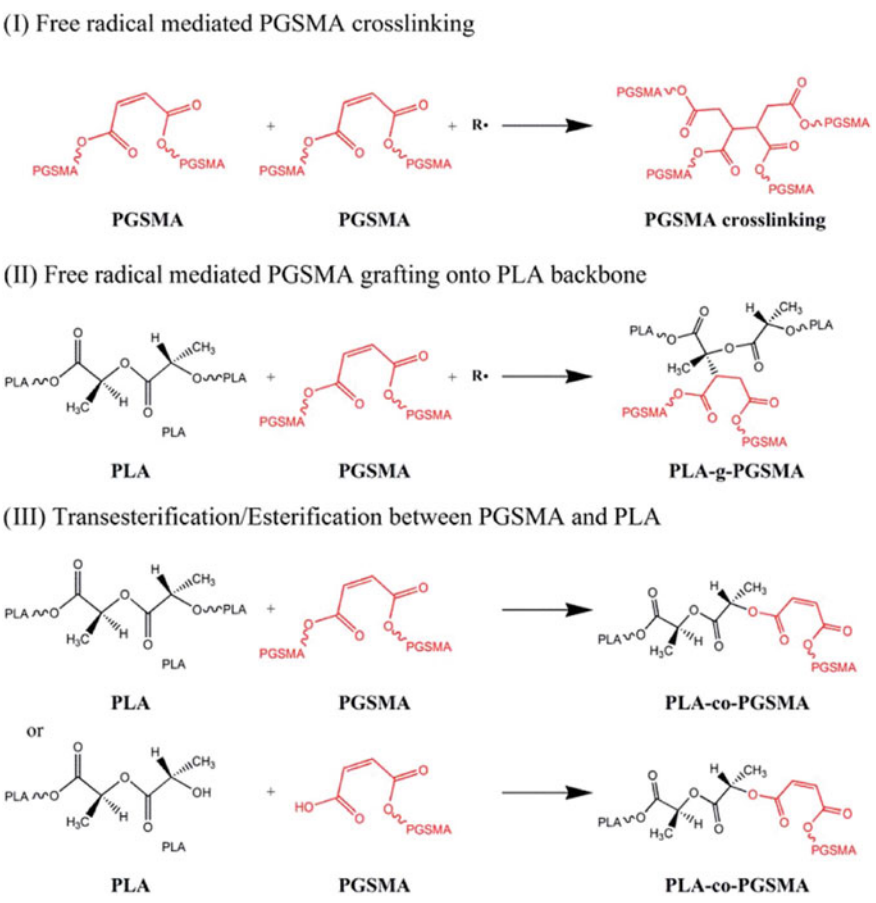

Fig. 5 Possible reactions between PLA and PGSMA on dynamic vulcanization process [80]. Open Access

The maximum elongation at break was obtained for ESO as compatibilizer reaching 130%; however, its tensile modulus and strength were lower than other compatibilizers (i.e., ESAO and AESO). This was attributed to the ESO acting as a plasticizer and also slightly induced interphase compatibilization through reaction of oxirane rings with hydroxyl groups in PLA, PHB and PCL. Regarding ESO, elongation at break reached a value of 65.8% with tensile modulus and strength reaching values similar to the blend compatibilized with ESO, i.e., 1.5 GPa and 35.4 MPa. The improvement of mechanical properties was ascribed to two phenomena: (i) the chemically modified soybean oils having more polar groups renders high solubility similar to that of biopolyesters, thus allow interaction between them which result in plasticization and (ii) the functionalities on the modified soybean (epoxy in ESO, epoxy and acrylate in AESO, and maleic anhydride in MSO) readily react with terminal hydroxyl groups

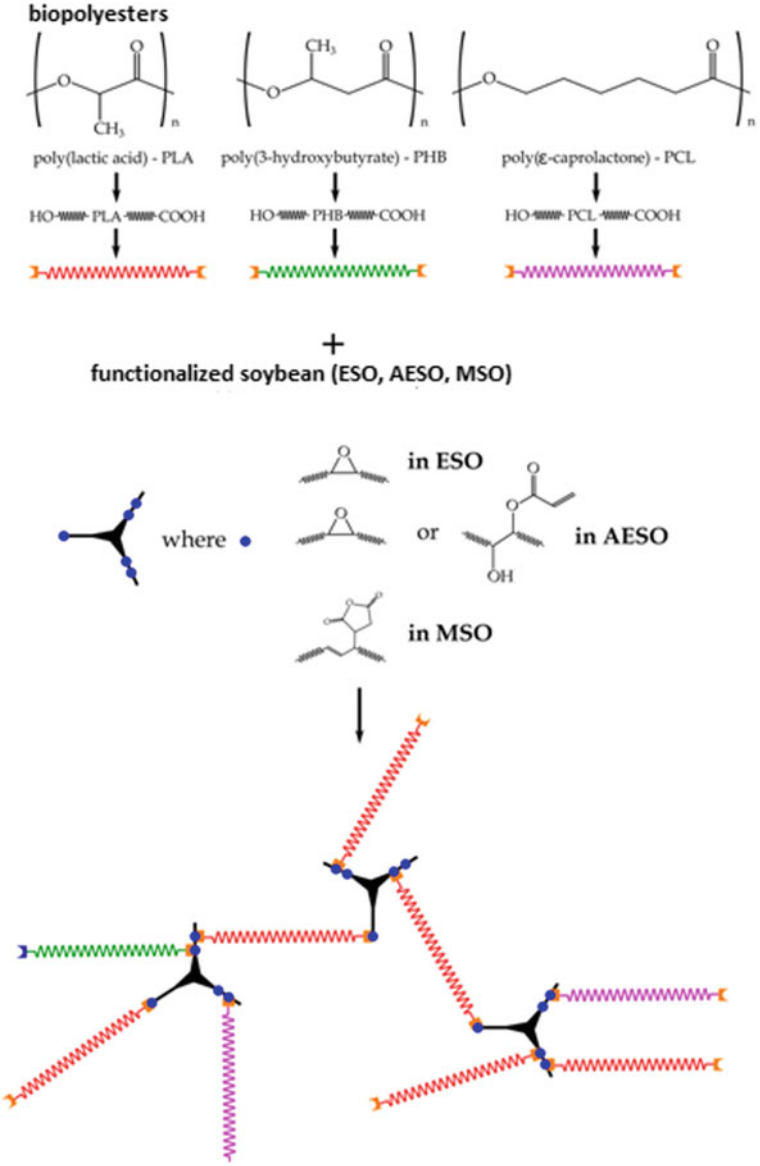

Fig. 6 Schematic representation of the possible reactions of biopolyesters with modified soybean oils [34]. Open Access

in all biopolyesters resulting in several processes such as chain extension, branching and/or cross-linking. The possible reactions of biopolyesters with modified soybean oils are shown in Fig. 6. A multifunctional vegetable oil, acrylated epoxidized soybean oil (AESO), as a compatibilizer for PLA was studied by Mauck et al. [51]. It was reported that AESO having acrylated groups were able to form cross-linking network at elevated processing temperature, while the presence of hydroxyl groups provided two routes for compatibilization of PLA/AESO blends viz (i) reactive compatibilization through the transesterification of AESO and PLA and (ii) synthesis of PLA star polymer with an AESO core. Furthermore, unmodified soybean oil (USO), AESO and 50/50 USU/AESO were investigated as a dispersed phase in PLA. It was stated that these additives improved the ductility of neat PLA while maintaining the T_g of neat PLA. The blend of PLA and AESO, USO, as well as PLA star exhibited a uniform oil droplet size distribution with small average droplet size and interparticle distance resulting in greatest enhancements of PLA tensile properties with no observable plasticization. The use of these natural-based products as compatibilizers is of the essence in a sense that most of the available compatibilizers are from crude oil which still adds to the current environmental burden. Epoxidized linseed oil (ELO) was recently reported as a suitable compatibilizer and plasticizer in work reported by Balart et al. [10]. It was found that ELO acts as a plasticizer and at the same time as a compatibilizer. This was confirmed by the good interaction between the filler and PLA as well as a decrease in storage modulus. On the other hand, the maleinized linseed oil (MLO) was also studied as a potential biobased plasticizer for biopolymers [31, 32]. Similarly, the presence of maleic anhydride can react with hydroxyl groups of the biopolymers and improve their ductility and/or interfacial adhesion in the case of blends. The synergistic effect of MLO on binary PLA/TPS blends at 30 wt% TPS was reported by Ferri et al. [31]. Elongation at break reached a value of 160% with detectable compatibilization using SEM, and T_g decreased by 10 °C with only 6 phr MLO. A multifunctional epoxy chain extender, Joncryl ADR 4368, as a compatibilizer of PLA/PBAT was investigated by Arruda et al. [8]. The presence of a chain extender improved adhesion between the phases which enhanced the ductility of the resulting product. Al-Itry et al. [2] reported that Joncryl during reactive extrusion links the polymer chains of the polymers improving its viscosity and molecular weight, hence improve the storage modulus of the resulting blend. It was stated that the storage modulus increased with increase in Joncryl content. Glycidyl methacrylate is the main group found in Joncryl, and its epoxy groups can interact with carboxylic as well as hydroxyl groups of the blend components which are hydrolyzed under heat and high shear stress. The effect of glycidyl methacrylate containing a random terpolymer of ethylene, acrylic ester (T-GMA) on the properties of PLA/PBAT blend was investigated by Zhang et al. [97]. It was found that the presence of T-GMA did not affect the tensile strength of the final product, while elongation at break increased up to 5 wt% of T-GMA. Similarly, the impact strength of PLA/PBAT (90/10) reached a maximum at 4 wt% of T-GMA. The improvement in mechanical properties was related to the reaction between epoxy groups and carboxyl or hydroxyl groups at the terminals of the polymer which enhanced the interfacial adhesion between PLA and PBAT. The addition of T-GMA also increased the stor-

age modulus, loss modulus and complex viscosity indicating improved melt stability during processing. Similar observations were reported by Kumar et al. [43]. The authors reported that the presence of T-GMA in PLA/PBAT blend improved the tensile modulus from 1254 MPa (PLA matrix) to 1746 MPa (in the case of PLA/PBAT blend with 5 wt% T-GMA), and the impact strength increased to 72.45%. This was related to the presence of T-GMA improving the interfacial adhesion between PLA and PBAT.

3.2 Nanoparticles Addition

Nanoparticles have also been incorporated in immiscible PLA blends not only to improve the interfacial adhesion but also to overcome the drastic reduction of tensile modulus and strength [54, 55, 87]. Odent et al. [55] investigated the compatibilization of PLA/poly(E-caprolactone-co-D, L-lactide(P[CL-co-LA] by adding nano-silica into blend system. Two preparation methods were used with regard to addition of the nano-silica particles: (i) addition of both P[CL-co-LA] and silica nanoparticles into PLA (one-step process) and (ii) addition of silica into one polymer (by dissolving polymer in chloroform followed by solvent evaporation) followed by extrusion with other polymer (two-step process). It was reported that oblong morphologies were observed in a two-step process where PLA was mixed with nano-silica and ten times improvement of impact strength was obtained (~27.3 kJ m^{-2} with only 5 wt% hexamethyldisilazane-modified silica (TS-530 compared to neat PLA 2.7 kJ m^{-2}). This method was then considered for further investigations into hydrophobic and hydrophilic silica nanoparticles viz. TS-530,225 m^2 g^{-1} and M-5200 m^2g^{-1} unmodified silica as well as H-5300 m^2 g^{-1} unmodified silica. The major fraction of silica nanoparticles was situated around P[CL-co-LA] dispersed phase and at the interface of the blend, regardless of silica-type. Furthermore, it was found that P[CL-co-LA] with spherical-like nodules disappeared after addition of 3 wt% of silica (regardless of surface functionalization) and oblong microstructure starts to appear, and the oblong micro-domains became interconnected at higher silica content resulting in co-continuous morphologies. The impact strength increased from 2.7 to 47.2 kJ m^{-2} after addition of 10 wt% P[CL-co-LA] and 5 wt% M-5 silica particles. The toughness was increased up to 18 times in the presence of silica nanoparticles, but the maximum content for nanoparticles to increase the toughness of the PLA-based blend material was 10, 5 and 3 wt% for TS-530, M-5 and H-5, respectively.

Cellulose nanowhiskers are natural-based fillers which have attractive properties such as good mechanical properties, abundant availability and low density. They can also be used as compatibilizers of polymer blends since their surface functional groups can be modified toward interaction with any material. Grafting of polymers which are miscible with PLA onto cellulose nanowhiskers can also be used as an alternative route to incorporate these fillers to overcome the drastic reduction of the young modulus and tensile strength of the resulting blend product [75].

Carbon-based materials are one of the most fascinating nanomaterials in recent years owing to their unique properties such as high mechanical strength, large surface area, high thermal stability (>700 °C), high aspect ratio (length to diameter) and electrical conductivity [12, 18, 86]. Multi-walled carbon nanotubes (MWCNT) as a compatibilizer for PLA-PCL blends were reported by Wu et al. [86]. In this case, MWCNT were functionalized with carboxyl groups and mixed with immiscible PLA/PCL blend which in turn improved compatibility between the two by reducing the size of dispersed PLA domain size (from 21.3 μm for neat PLA/PCL to 6.3 μm for blend nanocomposites) and enhancing the interfacial adhesion. This was attributed to a morphological structure that was formed in which MWCNTs were mainly dispersed in the PCL as well as an interface. The presence of MWCNTs improved rheological, conductive and mechanical properties when compared to neat PLA/PCL. Graphene oxide can also be used to compatibilize PLA/PCL blend as reported by Botlhoko et al. [18]. They thermally exfoliated and partially reduced graphene oxide (TERGO) by subjecting graphene oxide (GO) to thermal shock in a tube furnace at 700 °C for a minute under the flow of argon gas (120 ml min^{-1}). The compatibility between PLA and PCL was obviously improved by the addition of graphene oxide as evidenced by reduction of the domain size of the dispersed phase and increased interfacial adhesion. The dispersed PCL phase size in a PLA/PCL decreased from 1.31 to 0.76 μm in TERGO-filled blend composites, respectively. The improved compatibility was attributed to TERGO homogeneously dispersed in PCL resulting in an increase in viscosity ratio, which in turn leads to insufficient coalescence of the dispersed PCL droplets with only 0.05 wt% TERGO as shown in Fig. 7. The compatibilized blend (TERGO-filled blend composite) displayed balanced tensile modulus and strength and a significant increase in elongation at break when compared to neat blend and other composites Fig. 8. In the same way, the thermal conductivity and electrical were enhanced owing to of fairly pinched spherulites, a mixture of large and small spherulites (Fig. 9) or non-uniform dispersed PCL droplets (Fig. 7a) which act as electrical conducting pathways.

Clay nanoparticles were also studied as possible compatibilizers of biopolymer blends [16, 23, 57]. Ojijo et al. [57] evaluated the effect of clay (C20A) content (0–9%) compatibility between PLA and PBSA (70/30). A slight improvement in elongation was obtained at only 2 wt% of clay, and at this content (2 wt%), they obtained optimum properties. Functionalization of clay can also improve the interaction of clay with both blend components which in turn enhance interfacial adhesion as reported by Chen et al. [23]. In this study, clay was twice-functionalized (TFC) and it was found that the at low content the clay was fully exfoliated and located in the PLA phase, and the domain size of dispersed PBS did not significantly change, especially at low clay content (0.5 wt%). When the content of clay was increased, the clay layers were dispersed in both phases (PLA and PBS) and the domain size of PBS decreased to a certain level and increased gradually with the further increase of TFC. Two parameters were found to play a major role in these changes, (i) TFC act as compatibilizer because it bears the function that can react with PLA and PBS and (ii) some of the clay layers were situated at the interface of PLA/PBS preventing the coalesce of the dispersed domains and, therefore, contribute to the reduction in the

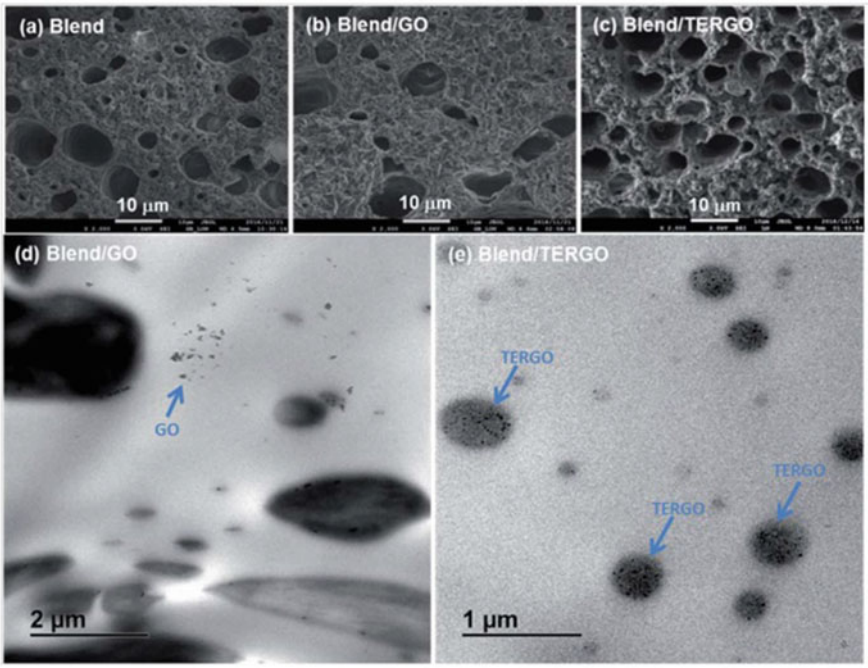

Fig. 7 Fractured PCL-etched surface morphology of the (**a**) neat blend, **b** GO-filled blend composite and **c** TERGO-filled blend composite. TEM images of (**d**) GO-filled blend composite and **e** TERGO-filled blend composite (the arrows show the position of GO and TERGO particles in blend matrix) [18]. Open Acess

domain size. Bitinis et al. [16] studied the effect of three different clays (unmodified clay (CNa^+) and two organomodified clays C15A and C30B) on the morphology of the PLA/NR blend. The addition of unmodified clay (CNa^+) did not influence the size of NR particle size (d ~940 nm), while organoclays significantly reduced the NR particle size (d ~560 and 306 nm, respectively) which led to homogeneous morphology with finer and uniformly dispersed rubber phase. It was also reported that the unmodified clay nanoparticles were agglomerated in PLA phase, while organoclays were located at the PLA/NR interface at low concentration (1 wt%). With further increase in clay content, C15A was preferably found to be located at the PLA/NR interface and NR phase because of the presence of a non-polar surfactant, while C30 preferred both interface and PLA phase. Thus there was a decrease in rubber particle size attributed to the compatibilizing effect of organoclays and a change in the viscosity ratio of the blend phases. At low organoclays content (1 wt%), the rubber particle was similar to pure PLA/NR blend and the clay preferably situated at the interface predominately acting as a compatibilizer, in this case, however, an increase in organoclays clay content led to the dominance of viscosity ratio. C30B in PLA increased PLA viscosity and facilitated the droplet breakup of the dispersed

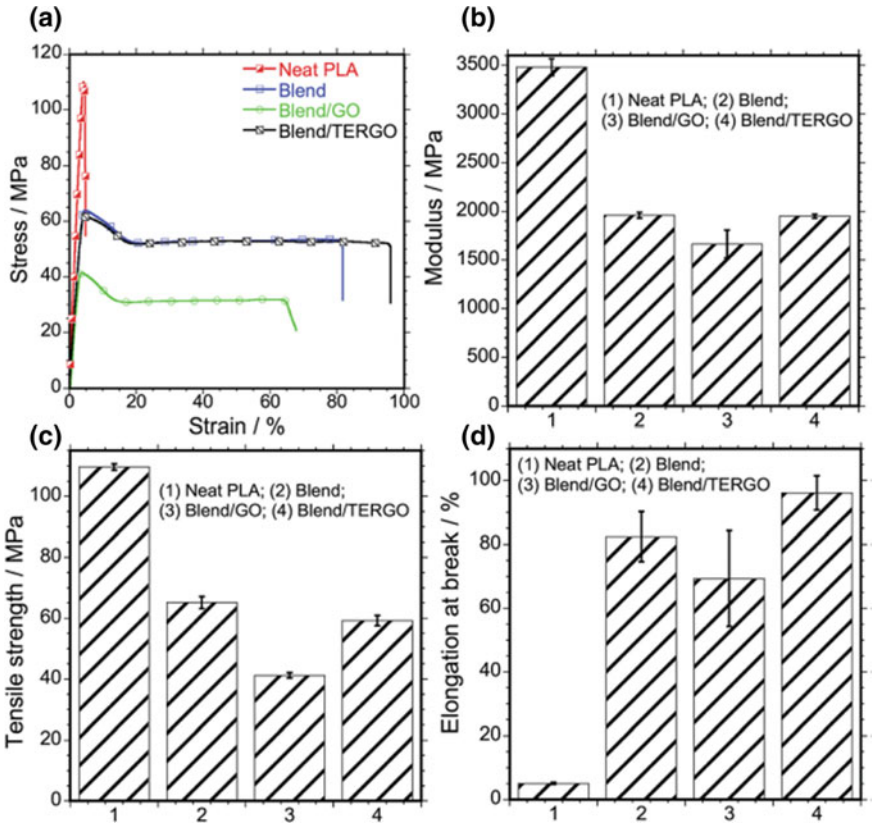

Fig. 8 **a** Stress–strain curves, **b** tensile modulus, **c** tensile strength and **d** elongation at break of neat polymers, blends and GO- and TERGO-filled blend composites [18]. Open Access

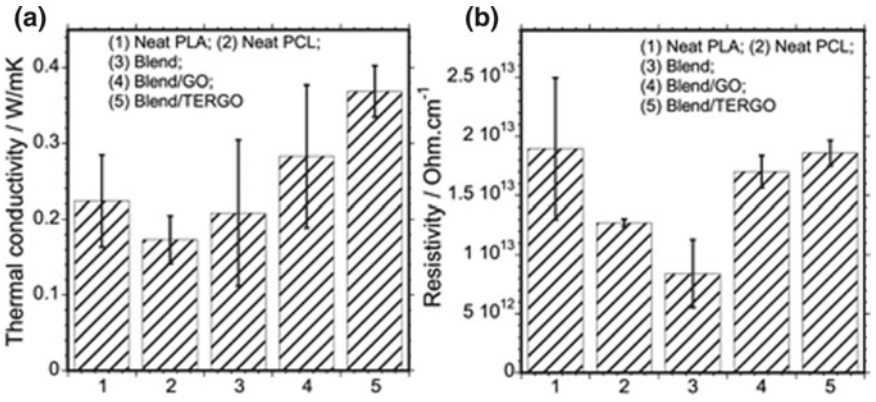

Fig. 9 **a** The thermal conductivity and **b** the electrical resistivity behaviors of neat PLA, PCL, blend, GO- or TERGO-filled blend composites. The filler loading was fixed at 0.05 wt% [18]. Open Access

high viscosity rubber phase resulting in a further decrease in rubber droplet size. In contrast, for C15A the rubber droplet size was not affected by an increase in clay content through their morphology appeared to be deformed and elongated at 5 wt%. The addition of C15A (1 wt%) led to a drastic increase in elongation at break reaching a value of 200% without changing tensile modulus and strength because of its location at the interface of PLA/NR. However, the strong interaction between C30B and PLA resulted in the more brittle blend. The addition of unmodified clay resulted in a drastic decrease of elongation at break, tensile modulus and strength because of poor dispersion.

3.3 Addition of the Third Polymer

Many efforts were focused on the compatibilization of PLA-based blends by adding a polymer which has functional groups that can afford formation of strong interfacial reaction between the components. The third polymer is usually selected based on the fact that it bears at least one functional group that can form strong interaction with PLA as well as another polymer [65]. In order to improve the interaction between PLA and poly[(butylenes succinate)-co-adipate)] (PBSA), [64] added various content of poly(butylenes adipate-co-terephthalate) (PBAT) (0–40 wt%). SEM image of fractured samples showed smooth surfaces for PLA (Fig. 10a), whereas for PBSA and PBAT samples elongated part of the ductile surface were observed Fig. 10b, c, respectively. However, the conventional phase separation for immiscible blends was established for PLA/PBSA blends without PBAT (Fig. 10d). PBSA was dispersed phase in PLA. The addition of PBAT led to a decrease in PBSA particle size due to less interfacial tension between PLA and PBSA in the presence of PBAT (Fig. 10e, f, g, h). The maximum tensile strength and impact strength of the blends were obtained at 20 wt% of PBAT. In another study, the authors used biopolymer as compatibilizers for PLA/PBAT with the aim of replacing the commonly used inorganic non-degradable compatibilizers [65]. The blend ratio was kept at 70/30 while biopolymers (PBS, PBSA and PHBV) were varied from 1 to 5 phr. It was reported that elongation at break increased for only 1 and 3 wt% of PHBV, while a decrease was observed for other biopolymers. This was attributed to other biopolymers acting as nucleating sites which increased the crystallinity of the one polymer which results in phase separation. In the case of impact strength, an increase was observed only for 1 wt% of PHBV, whereas other biopolymers showed a decrease in impact strength with an increase in their content.

4 Opportunities and Future Remarks

PLA and PLA blended with other biopolymers have the potential of replacing petroleum-based polymers in various applications such as packaging and biomedical

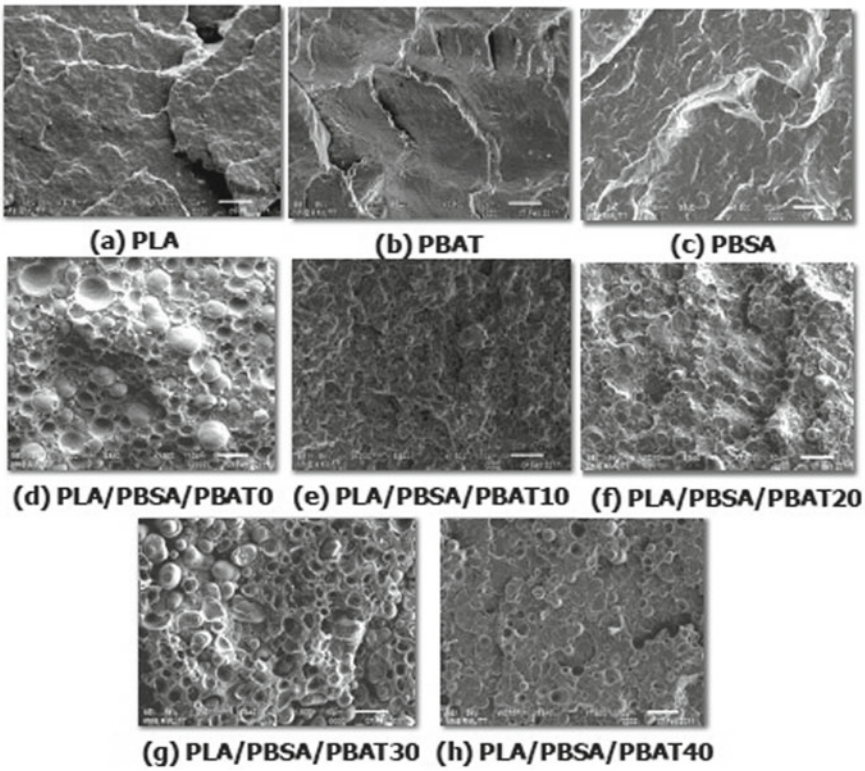

Fig. 10 SEM images of neat PLA, neat PBSA, neat PBAT and their blends with PBAT 0–40 wt% [64]. Open Access

application owing to their unique properties such as biodegradability and renewability. There are, however, some concerns that need to be addressed in order for them to be competitive with a petroleum-based polymer which offers new research opportunities. The techniques used to improve the toughness of PLA such as biobased plasticizers need some developments with regard to their volatility at high processing temperatures since they have low molecular weight. The addition of thermally stable groups to prevent the loss of these compounds is important to afford supertough PLA-based blends. The understanding and prediction the migration of the nanofillers when PLA is blended with other biopolymers are essential in order to control their localization are still in its infancy stage. Models which can predict the migration of the fillers are of significant importance in order to understand and design the system in which nanofillers can be driven into the interface of the blend components to promote interfacial adhesion [28]. Most of the copolymers are still obtained from non-renewable resources which add to the current environmental crisis. Furthermore, these copolymers are usually synthesized prior blending which is undesirable for industrial production and/or applications; hence this calls for novel

ideas to develop advanced technologies that can produce these materials without using complex conditions to afford their large-scale production.

5 Conclusion

From the arguments presented in this chapter, PLA blending with other biopolymers is the most cost-effective method to modify the brittleness of PLA; however, most of the available polymers are immiscible with PLA. This limits the application of PLA-based blends in high-end applications. The compatibility strategies such as copolymerization and addition of fillers have been applied to improve the compatibility of PLA with other polymers. Chemical polymerization is an effective method to promote interfacial adhesion between PLA and other biopolymers, however, is costly. This process is still limited to lab-scale and involves polymerization prior to blending. Therefore, more studies are still required for the development of this technique to afford their production at industrial scale. Addition of nanoparticles serve as a promising strategy since it does not contribute only to the compatibility of the components but compensate for the reduction of tensile modulus and strength introduced by plasticization of the incorporated polymers. Again, these nanoparticles offer an opportunity to add novel functionalities to the resulting product which broadens the application of the resulting blend composite.

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Chapter 4
Biocomposite Reinforced with Nanocellulose for Packaging Applications

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1 Introduction

Food packaging is one of the most important areas in food technology dealing with the protection and preservation of all types of foods from microbial contamination and oxidative damage. In addition, packaging reduces food loss and increases the shelf life of food leading to a decreased economic loss for the distributor and consumer. Around 50% of agricultural produce are ruined due to the lack of packaging. Presently, the plastics that are commonly used in different packaging field are developed from petroleum-based products. However, these packaging materials are a threat to the environment as they are non-biodegradable, and they remain in the environment for 100–450 years [1]. At present, the technique used to manage the plastic wastes are burning and recycling; however, it is not enough for solving the environmental problems. An effort has been taken to decrease the waste disposal during the maintenance of food quality, as well as the production of eco-friendly packaging film using renewable sources. The increasing petroleum prices have also led to the search for an economical method for the development of packaging materials. Furthermore, there is a constant consumer demand to develop packaging materials that are biodegradable, as well as eco-friendly [2], thus encouraging researchers and industries to develop packaging materials derived from natural biopolymers. The natural polymers market value improved from 0.4 to 1.3 billion pounds in the year 2006–2013 [3]. To attain this growing trend, there is a need to venture resources that are sustainable and renewable. By the way, polysaccharides such as chitosan (CS)

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and cellulose are the most important since these two are the most abundant natural polymer.

2 Chitosan

Chitosan is a natural polysaccharide derived from chitin that consists of *N*-acetyl glucosamine and D-glucosamine [4]. Chitosan is insoluble in water but only soluble in aqueous acidic solution which restricts its use. Chitosan has various exciting physicochemical and biological properties like biocompatibility, biodegradability, and non-toxicity, which makes CS more appropriate for use in many applications, like complementary foods, ingredients, drug delivery, wastewater treatment, cosmetics, and postharvest preservation of fresh produce [5, 6].

Generally, biopolymer-based packaging films are more sensitive to the environmental situation and usually have poor mechanical properties. To solve this problem, various researchers developed blend film based on the combination of biopolymers and synthetic polymers [7]. Poly(vinyl alcohol) [PVA] has been extensively used for the development of composites by blending with various natural polymers [8].

3 Polyvinyl Alcohol

The PVA is a water-soluble, semi-crystalline polymer widely used because of its excellent physical characteristics, which arise owing to the presence of hydroxyl groups and the formation of hydrogen bond [9]. It has good biodegradability, excellent resistance to chemicals, and better mechanical behavior [10]. Conversely, the usage of biopolymers for packaging of foods is still challenging due to its poor physical properties. The addition of nanocellulose (NC) as fillers to these composites might augment the physical properties. This paves a way for use of cellulose as a by-product of agricultural waste for the application in food industries.

4 Cellulose

Cellulose is one of the most plentiful natural biopolymers, which is actually prepared from plants sources and other novel resources of bacteria and tunicate [11–14], among which, the cotton fibers are most important fibers for the production of cellulose and nanocellulose. The fibers are primarily made up of three constituents like cellulose, hemicellulose, and lignin [15, 16]. Conversely, hemicellulose and lignin compounds are comparatively amorphous and cellulose material is more crystalline in nature [17]. The cellulose has both crystalline and amorphous section. Cellulose has a strong and long-chain polymer that are tightly arranged with inter- and intramolecular hydrogen

bonding during the van der Waals forces [18, 19]. Cellulose microcrystals (CMCs) hold better mechanical behavior, as well as very cheap, low density, hydrophilicity, chirality, biodegradability, low thermal enlargement, and less toxicity [20–22].

Cellulose is one of the most commonly available biopolymer globally, which is renewable and biodegradable. Cellulose is a natural polymer consisting of D-glucose in chain form (Fig. 1). Mostly, it is existing in the form of pure cellulose in cotton, whereas, in wood and plant materials, it is available in a combined form with lignin and hemicelluloses. Mechanical and chemical treatments of cellulose result in more valuable materials like CNC and CNF. The CNC has good mechanical properties, thermal behavior, aspect ratio, eco-friendly, and low cost [23]. CNC comprises of the highly crystalline rod-like structure with a large specific area and length in the range of tens to hundreds of nanometers and 1–100 nm in diameter [24]. Moreover, CNC holds ample of OH groups on its surfaces, creating a hydrophilic nanomaterial that may enable their diffusions in the water-soluble polymer matrices [25]. Earlier, some researchers have stated the use of nanofibers from agricultural residue as reinforcement in polymer matrices such as CS [26] and PVA [27].

5 Nanocellulose

With the progress of nanotechnology, cellulose is the most important natural biopolymer on earth, which gains more attention in the form of nanocellulose (Fig. 2). Based on the size and shape, NC is grouped as CNC, cellulose nanofibers (CNF), and bacterial cellulose [BC] [28, 29]. The lignocellulosic fibers acquired from agricultural residues have a great importance due to its abundance, low cost, renewability, and biodegradability [30]. The plant fibers containing relatively high cellulose content make it an attractive material for the use in the development of biocomposites that may efficiently reduce the environmental pollution, saving the limited forest and petroleum resources, and thus encourage the added value of agricultural waste fibers.

CNC and CNF can be obtained from the same cellulose source by two different methods (Fig. 3). CNC can be prepared by acid hydrolysis of wood fiber or any other

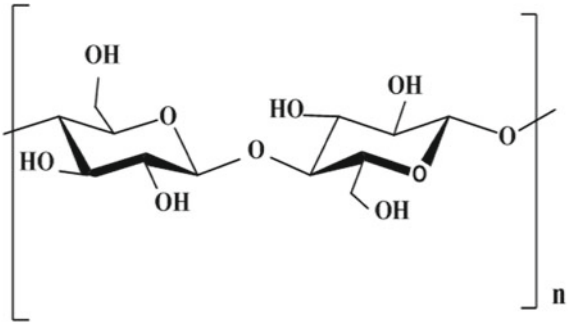

Fig. 1 Cellulose structure

cellulosic materials, resulting in a rod-like nanoscale structure with 3–20 nm width and 50–500 nm in length [31]. CNF can be produced using mechanical processes, with or without chemical and biological treatments, yielding 4–50 nm width and greater than 500 nm in length of linear or branched chains [31]. In addition to CNC and CNF, there are two more types of cellulose nanomaterials: microcrystalline cellulose (MCC) consisting of purified and partially depolymerized cellulose particles with an average degree of polymerization between 200 and 450 and microfibrillated cellulose (CMF), obtained from cellulose fibers which are submitted to high mechanical shearing forces.

5.1 Cellulose Nanocrystals

The CNC is a natural biological polysaccharide, having great potential in many applications due to its various key properties, e.g., better tensile and modulus value, high surface area, good optical properties, eco-friendly, and good biodegradable properties [33]. Usually, CNC has been described as reinforcing filler for the production of polymer composites [34, 35]. Nanocellulose is commonly used as a reinforcing agent; however, they might also be used as matrixes for several types of composites including films for the applications of food packaging.

Generally, CNCs can be synthesized from many sources, like plants [36, 37], animals [38], and bacteria [38–41]. Recently, numerous agricultural and industrial residues have gathered much interest in the production and utilization of CNC; these residues include sugarcane bagasse [42], rice husk [43], rice straw [44] and wastepaper [45, 46].

CNC is a derivative of cellulose which comprises of nanofiber, which determines the product characteristics and its functionality. The nanofibers are very useful material for the development of low cost, lightweight, and strong nanocomposite materials [47]. Usually, CNC is prepared by the bioformation of cellulose via bacteria as well as by the breakdown of plant celluloses using shear forces in refiner techniques.

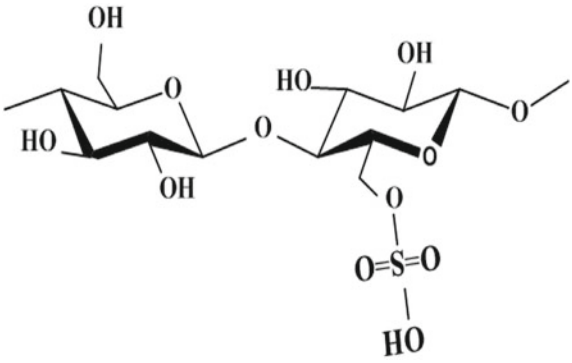

Fig. 2 Chemical structure of nanocellulose

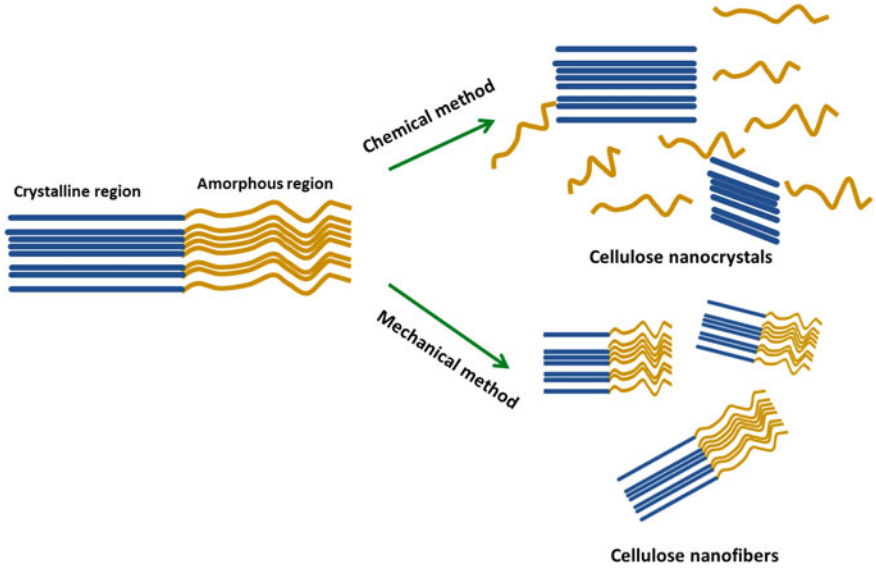

Fig. 3 Mechanism of chemical and mechanical methods for producing the CNC and CNF [32]

CNC derived from wood pulp can also be produced by electrospinning [48] or by controlled acid hydrolysis of bleached fibers [49].

5.2 Cellulose Nanofibers

CNF is documented as more efficient materials than microfibers to strengthen the composite because of their interactions between the nanomaterials which may form a percolated network formed by hydrogen bonds, only if there is a good dispersal of nanofibers in the composites and their large specific area in the arrangement of various 100 m^2/g. It is expected that NC as reinforcing filler in the composites could offer value-added particles with greater characteristics and wide applications for the next generation of biodegradable materials. CNC is likely to exhibit better stiffness since the tensile modulus of the CNC is as high as 134 GPa. The tensile strength of the CNC was evaluated to be nearly 0.8 up to 10 GPa [50–52]. Polymer matrices are the combinations of polymers with inorganic or organic materials holding particular geometries like fibers, flakes, spheres, and particulates. The usage of nanofillers is leading to the production of polymer composites and denotes a radical substitute to the conventional polymer nanocomposites [53].

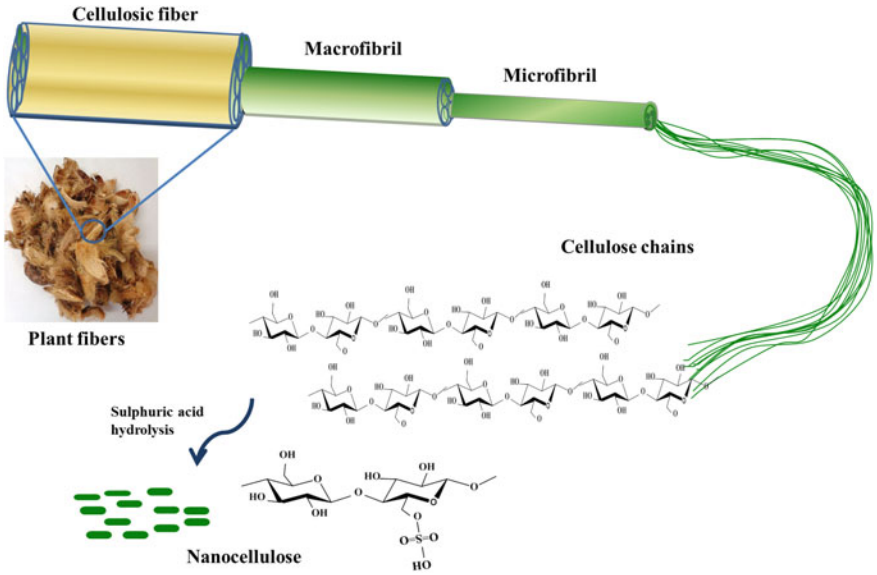

Fig. 4 Synthesis of nanocellulose from cellulosic fibers [103]

5.3 *Bacterial Cellulose*

Previously, bacterial cellulose (BC) is produced in the form of nanomaterial by *Gluconacetobacter* species which is grown in a medium containing carbon and nitrogen sources. Though it is chemically similar to plant cellulose, BC is formed as a bottom-up process, in that the bacteria produce cellulose and form a bunch of nanofibrils and gathering of a nano-sized ribbon-shaped fibrils in the range of 70–80 nm width [54] preparing a pellicle membrane which has a water-holding capacity of 60–700 times its dry weight [55]. The BC is also synthesized in pure form which is not combined with hemicellulose and lignin components, decreasing the purifying costs and environmental pollutions resulting from the usage of harsh chemicals reagents [56]. It might also be used to prepare composites in various methods.

5.4 *Preparation of Nanocellulose*

Various techniques have been stated for the isolation of NC fibers from agricultural residues (Table 1). Alemdar and Sain [57] synthesized CNF from agricultural wastes like wheat straw and soy hulls to utilize as reinforcing filler in biocomposites by the chemo-mechanical method. Fahma et al. [58] prepared CNF by hydrolyzing oil palm empty fruit bunch (OPEFB) with H_2SO_4 hydrolysis (Fig. 4). They noted a decline in crystallinity and degree of polymerization during the acid hydrolysis.

Table 1 Preparation of nanocellulose from different sources and various methods

Methods for obtaining CNC	Cellulose source	Nanocellulose	Particle size (nm)	References
H_2SO_4 acid hydrolysis	Sugarcane bagasse	CNC	5 ± 1.1, 275 ± 73	Achaby et al. [42]
Enzymatic hydrolysis	Sugarcane bagasse	CNC	14–18, 193–246	Camargo et al. [63]
Acid hydrolysis	Red algae	CNC	5.2–9.1, 285.4–315.7	Achaby et al. [27]
H_2SO4 hydrolysis	Rice straw	CNC	3–11, 39–117	Lu and Hsieh [12]
H_2SO4 hydrolysis	Rice husk	CNC	10–15	Johar et al. [43]
H_2SO4 hydrolysis	Cassava bagasse	CNF	2–11, 360–1700	Teixeira et al. [64]
H_2SO4 hydrolysis	Grain straws	CNC	10–25, 120–800	Oun and Rhim [65]
H_2SO4 hydrolysis	Kenaf bast fibers	CNC	12, 158	Kargarzadeh et al. [66]
H_2SO4 hydrolysis	Kenaf fibers	CNC	12 ± 3.4, 70–190	Zainuddin et al. [67]
Acid hydrolysis (H_2SO4 and HCl) and ultrasound assisted extraction	Waste cotton cloth	CNC	3–35, 28–470	Wang et al. [68]
H_2SO4 hydrolysis	Industrial waste cotton	CNC	10 ± 1, 180 ± 60	Thambiraj and Ravi Shankaran [69]
Chemo-mechanical fibrillation via griding and homogenization	Areca nut husk fibers	CNF	1–10	Chandra et al. [30]
H_2SO_4 hydrolysis and chemical, enzymatic pretreatment	Barley straw and husk	CNC	5–15, 40–270	Fortunati et al. [70]
H_2SO_4 hydrolysis, Microbial degradation	Okra fibers	CNC	–	Fortunati et al. [71]
H_2SO_4 hydrolysis	Kiwi pruning stalks	CNC	10–15, 100–150	Luzi et al. [72]

(continued)

Table 1 (continued)

Methods for obtaining CNC	Cellulose source	Nanocellulose	Particle size (nm)	References
H_2SO_4 hydrolysis	Cotton	NCC	25, 450,	Shamskar et al. [73]
Ethanol and peroxide + ultrasonication	Wood	CNC	1 ± 9, 500	Li et al. [74]
H_2SO_4 hydrolysis	Hemp	CNC	1–4.5, 20–120	Luzi et al. [75]
NaOH and H_2SO_4 hydrolysis	Miscanthus giganteus	CNC	8.5, 2.8	Cudjoe et al. [76]
NaOH and H_2SO_4 hydrolysis	Ramie fibers	CNC	3–15, 100–300	Habibi et al. [77]
H_2SO_4 hydrolysis	Sugarcane	CNC	20–60, 250–480	Kumar et al. [78]
H_2SO_4 hydrolysis mechanical treatment	Wheat straw	CNF	30–70, 90–110	Kaushik et al. [79]
H_2SO_4 hydrolysis	Tunicate	CNC	30–40, 500–3000	Roman and Gray [80]
Enzymatic hydrolysis	Tunicate	CNC	16.04	Zhao et al. [81]
NaOH and H_2SO_4 hydrolysis, steam extraction	Coconut coir fiber	CNF	5–50	Abraham et al. [15]
H_2SO_4 hydrolysis	Soy hulls	CNC	4.9, 503	Neto et al. [82]
H_2SO_4 hydrolysis	Mengkuang leaves	CNC	5–25, 5–80	Sheltami et al. [83]
H_2SO_4 hydrolysis	Corncob	CNC	4.15, 210.8	Silvério et al. [84]
H_2SO_4 hydrolysis	Bamboo fibers	CNC	5–8, 100–130	Brito et al. [85]
H_2SO_4 hydrolysis	Banana pseudostem	NCC	1.9–7.2, 12–135	Pereira et al. [86]
Acid and ball milling methods	Sugarcane bagasse	CNC and CNF	160–400, 20–30	Sofla et al. [32]
Chemo-mechanical method	Wheat straw and soy hull	CNF	10–120	Alemdar and Sain [57]

(continued)

Table 1 (continued)

Methods for obtaining CNC	Cellulose source	Nanocellulose	Particle size (nm)	References
H_2SO_4 hydrolysis	Oil palm empty fruit	CNF	10–80	Fahma et al. [58]
Chemo-mechanical method	Oil palm empty fruit	CNF	5–10	Fatah et al. [59]
Chemical ultrasonic method	Wood, bamboo, wheat straw and flax fibers	CNF	10–40	Chen et al. [60]
TEMPO oxidation mediated system	Hardwood celluloses	CNF	3–4	Saito et al. [61]
Chemical, grinder and homogenizer method	Coir	CNF	18–20	Kanoth et al. [87]
H_2SO_4 hydrolysis	Rice straw	CNC	15 ± 1.3	Anand babu et al. [88]
H_2SO_4 hydrolysis	Cotton wool	CNC	–	Popescu [89]
Chemo-mechanical process	Cotton fibers	NCF	70–300	Savadekar et al. [90]
Grinding and homogenization	Kenaf fibers	CNF	15–80	Jonoobi et al. [91, 92]
Disintegration in a Waring blender; homogenization, TEMPO	Sugar beet pulp	NC	–	Habibi and Vignon [93]
Enzymatic pretreatment, high shear refining, cryocrushing	Bleached kraft pulp	CMF	100	Janardhnan and Sain [94]
Mechanical pretreatments followed by homogenization	Rubber wood	CNF	10–90	Jonoobi et al. [92]
Mechanical pretreatments followed by homogenization	Empty fruit bunches	CNF	5–40	Jonoobi et al. [92]
Homogenization	Swede root	CMF	–	Bruce et al. [95]

(continued)

Table 1 (continued)

Methods for obtaining CNC	Cellulose source	Nanocellulose	Particle size (nm)	References
Substrate media	Bacterial cellulose	CNF	40–70	Castro et al. [96]
H_2SO_4 hydrolysis	Bacterial cellulose	CNC	50, 100–1000	Grunert and winter [97]
H_2SO_4 hydrolysis	Bacteria	CNC	10–50, 100–1000	George et al. [98]
HCl hydrolysis	Bacteria	CNC	15–25, 160–420	George and Siddaramaiah [99]
HCl hydrolysis	Cotton	CMC	5–10, 100–150	Araki et al. [100]
Steam explosion treatment and hydrolysis	Sunflower stalk	CNC and CNF	5–20, 150–200	Fortunati et al. [101]
Ultrafine grinding	Sludge (residue from dissolving cellulose production)	CNF	100	Jonoobi et al. [102]

Fatah et al. [59] reported a chemo-mechanical method to extract CNF from OPEFB and successfully achieved in attaining the CNF with a diameter ranging from 5 to 10 nm and observed a decrease in the crystallinity that is inclined by the pressure of mechanical method. The chemical ultrasonic technique was reported by Chen et al. [60] for the extraction of CNF from four different fibers such as wood, bamboo, wheat straw, and flax fibers. The authors successfully isolated the nanofibers with a diameter in the range of 10–40 nm from bamboo, wheat straw, and wood fibers; however, flax fibers with rich content of cellulose were not nanofibrillated evenly. Saito et al. [61] presented a pretreatment of cellulose by oxidation with 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated method. They extracted CNF in the range of 3–4 nm in width from hardwood celluloses. The defibrillation of nanofibrillated cellulose generally involves various mechanical techniques like cryocrushing, microfluidization, high-intensity ultrasonication, grinding, and high-pressure homogenization [62].

Kanoth et al. [87] synthesized nanofibrillated cellulose with the diameter of 18–20 nm from coir with the help of a commercial grinder to prepare the pulp followed by a chemical process. For the nanofibrillation of chemically pretreated and bleached pulp, an ultrahomogenizer was utilized.

5.4.1 Acid Hydrolysis

Sulfuric acid (H_2SO_4) is the most frequently used acids for the extraction of CNC. It is more stable than any other organic acids, and it can offer a better effect on hydrolysis. The CNC was evenly distributed during H_2SO_4 hydrolysis because its sulfate ion shows negative charges and could create an electrostatic repulsion between CNC particles [86]. However, H_2SO_4 is a strong oxidizing acid. The greater thermal degradation of cellulose generally happens when sulfates are introduced on the surfaces of cellulose during hydrolysis, mainly at maximum temperature, which leads to lesser yields of CNC, resulting in a negative impact on the manufacturing in the large-scale and CNC application. Due to these motives, growing efforts have been made to utilize other acids to substitute H_2SO_4 for the cellulose hydrolysis in recent periods. Hydrochloric acid (HCl) has the weak oxidizing capability and less thermal degradation of CNC leading to poor dispersal capability for CNC. The combination of H_2SO_4 and HCl may be a good option for the extraction of CNC. The HCl hydrolysis may improve the CNC dispersion property by the electrostatic repulsion of sulfate during the mixed acid hydrolysis.

Martins et al. [104] stated that the acidic hydrolysis is the common method used for the isolation of cellulose nanowhiskers (CNW), which could be performed using H_2SO_4 or HCl. In this method, the crystalline parts are insoluble in acid, under the conditions used for isolation. The isolation procedure and the source of cellulose are tremendously influent on the morphology and other properties of CNW; hence, selecting the hydrolysis method to be used becomes an important stage in the successful isolation of nanocrystals. It is well known that the utilization of different acidic solutions might cause variations in the stability of the colloidal suspension, because of the presence of different loads on the surface of fibers. The use of H_2SO_4 for isolation leads to the introduction of negative sulfate groups on the outer crystals surface during the hydrolysis process and considered that it is responsible for the stabilization of crystals in the resultant solution, although the presence of sulfate groups might cause the decrease in thermal stability, as a large amount of sulfate groups on the cellulose lead to decreased thermal degradation of the cellulose. If HCl is used instead of H_2SO_4 to hydrolyze the cellulose, the thermal stability of the obtained nanocrystals is enhanced; however, the nanocrystals are likely to aggregate due to the lack of electrostatic repulsion force between the particles, resulting in an unstable solution [104].

The isolation of CNW by acid hydrolysis might cause digestion of the pretreated fiber structure amorphous region, resulting in crystalline nanoparticles [105]. Siqueira et al. [106] explains the principle of the amorphous regions of cellulose disruption, to produce CNC. The hydronium ions can pierce into the amorphous domains which promote the hydrolytic cleavage of glycosidic bonds liberating individual crystallites [107].

Similarly, Siqueira et al. [106] studied the influence of the use of H_2SO_4 or HCl to extract stable suspensions of CNC. However, the H_2SO_4 might produce more stable suspensions when compared to the HCl because it results in CNC with marginal loading area and the CNC obtained by H_2SO_4 hydrolysis has a negatively charged

surface due to esterifying the hydroxyl groups of the surface for generating the sulfate groups.

Johar et al. [43] mentioned in the reports that the process should ultimately decrease the size of the micro fibers to nanoscale level. The resulting nanoparticles are in the range of 15–20 nm in diameter and aspect ratio of 10–15 nm.

5.4.2 Ultrasound

The very simple and effective method for valuable recycling and degradation of cellulose wastes includes hydrolysis and ultrasonic degradation. Oksman et al. [108] compared the CNW obtained by ultrassonification, homogenization, and acid hydrolysis. The degree of crystallinity of the materials was 73% after ultrasonification, 77% after homogenization, and 75% after acid hydrolysis. This study concluded that the nanowhiskers produced by mechanical methods have good thermal stability compared to the chemical treatment. On the other hand, this stability is not greater than the thermal stability of native cellulose because the cellulose chains are shorter and might have a lower degree of polymerization. But, the dimensional of residues extracted by sonication and homogenization was 10 nm in sizes. Thus, the ultrasonification, homogenization, and grinding processes have gained more attention to the extraction of micro- and nanofibrils [109]. Additionally, the ultrasonic-assisted hydrolysis method has been confirmed to be more effective to enhance the productivity of CNC [110, 111].

5.4.3 Oxidation Mediated 2,2,6,6-Tetramethylpiperidine-1-Oxyl (TEMPO)

The nanofibrillated cellulose can be obtained through oxidation method using TEMPO and consequent mechanical dispersion in water. This technique has some important characteristics: The final material could be dispersed in water, with all individual fibrils having a uniform width of 3–4 nm. Also, there is plentiful presence of carboxylate groups on the surface of cellulose fibrils (~1.7 nm) by which the electrostatic repulsion or working of the osmotic behavior is efficient between the fibrils produced by this method anionically charged water [112–114]. Iwamoto et al. [114] described that the wood pulp oxidation by radical TEMPO which acts as a catalyst in an aqueous medium with sodium hypochlorite and sodium bromide at pH 10 might cause the development of C6 carboxylate groups on the surface of microfibrils, retaining the original crystallinity of cellulose I and the crystal width.

The films developed by TEMPO oxidation of CNF dispersed in water have better properties like good transparency and resistance to elasticity, low thermal expansion, and low oxygen permeability [114, 115]. Fukuzumi et al. [113] isolated CNF with an average width of ~4 nm, but with different lengths: 200, 680, and 1100 nm by TEMPO oxidation method. By examining the viscosity, average degree of polymerization (DPV) for individual CNF obtained was found to be 250, 350 and 400, respectively.

The nanofibrils having short length result in fewer DPV values; however, it has good light transmittance. In contrast, nanofibrils are in greater length and result in better tensile strength and elongation at break for the film. The barrier properties of all the films with different CNF lengths may differ, in which the nanofibrils with maximum length showed good oxygen barrier properties. However, in the case of water vapor permeability, the CNF length does not show any significant effect and mostly inclined by the water vapor transmission rates (WVTR) film.

Fukuzumi et al. [115], successfully isolated the nanofibrils from bleached kraft pulp prepared by TEMPO oxidation. The subsequent treatment with various calcium solutions was performed to exchange the ions by converting the carboxylate groups. The nanofibrils subjected to various treatments might improve the thermal behavior of CNF.

5.4.4 Mechanical

The CNF isolated by mechanical method provides some advantages than chemical treatment methods. The mechanical method being an environmentally friendly method does not involve the use of solvents or any other chemical reagents. Furthermore, the produced material can be used as reinforcement in polymer matrices [116, 117]. The mechanical methods utilize energy during its performance, however, make use of all wood materials for the production of CNF, whereas during the chemical method, almost half the wood becomes pulp and other half is dissolved [118].

Mtibe et al. [117] studied a comparison between two forms of isolation of corn stover CNF, by acid hydrolysis and mechanical method. Primarily, the waste was treated by basic procedure, then the pulp of cellulose was collected, and finally, it was subjected to these two methods. The mechanical method comprises of two steps: At first, the natural fiber was processed into a mechanic mixer and consequently passed through a mechanical grinder. By evaluating the results of both the nanofibers and nanowhiskers prepared by mechanical and chemical treatment respectively, it was noted that the dimensions of CNF were 4–10 nm in diameter and length in few microns, whereas chemically treated CNW had a dimension between 3–7 nm in diameter and 150–450 nm in length. Regarding the crystallinity data, the CNF exhibited 66.4% of crystallinity, but for the CNW, it was 72.6% of crystallinity. The degree of crystallinity is less because of the mechanical method used to break the crystalline domains of the cellulosic fibers. As for the mechanical behavior, the obtained CNF by mechanical technique indicates the enhancement of the stress transfer fiber to fiber that explains the increase in the mechanical and thermal behavior of the material, with better stability [117].

Ardanuy et al. [11] reported the elimination of amorphous phase of cellulose to form a crystalline CNC in the range of around 2–20 nm in diameter and 100–600 nm in length. The CNC might be utilized as reinforcing filler for the development of functional nanomaterials, antimicrobial films, protective coatings, polymeric nano-

biocomposites, food packaging films, drug delivery, and membrane filters and substrates for flexible electronics [119–121].

Robles et al. [122] illustrated the variations of polylactic acid (PLA) behavior after the application of CNC obtained from blue agave. They observed that the different methods of producing the cellulose in nanoscale can provide various characteristics to the obtained composite, like enhanced mechanical behavior and hydrophobicity due to the non-polar covalent bond formation between the hydroxyl groups and free coupling which also improves the dispersion within the matrix that is important in producing the materials with good water barrier property.

5.4.5 Enzyme Hydrolysis

Enzyme hydrolysis is the new technology based on the use of hydrolytic enzymes alone or in combination with some other organic chelating compounds. This approach is now a very popular method to perform the pretreatment of the lignocellulosic materials. The aim is to purify the cellulose from other interfering compounds like lignin and hemicellulose, prior to its final acid hydrolysis which results in CNC [123]. The enzymatic pretreatments are more particular than the chemical treatment and have minimal effect on the surroundings. The use of enzymes like pectinases and cellulases has gained more attention for their capability in eliminating the water-soluble material, minerals, pectin, and amorphous hemicelluloses, etc. [106].

Fortunati et al. [70] explained that CNC was successfully isolated from both barley straw and husk by approaching two different methods: an alkaline and enzymatic pretreatment, followed by an acid hydrolysis. The results prove the efficacy of the enzymatic pretreatment on the value of resultant CNC. The outcomes showed that chitosan decreased the optical transmittance and the mechanical properties of PVA matrix, while its combination with CNC, particularly when isolated by enzymatic pretreatment and incorporated at a higher concentration, was capable to modify the optical transparency, and the mechanical and thermal behavior. In the case of enzymatically pretreated fibers, the defibrillation procedure appears to be more effective and certain coils, noticeable as vascular protoxylem arrangements were observed. They were visible because of the more efficient elimination of hemicellulose and lignin compounds.

Cellulases are complexes of endo-glucanases, exo-glucanases, and cellobiohydrolases. These enzymes act synergistically in the cellulose hydrolysis. Endo-glucanase enzymes randomly attack and hydrolyze the amorphous region of cellulose at the same time as exo-glucanase break down the polymer chain of cellulose either in the reducing ends or non-reducing ends. Cellobiohydrolases hydrolyze the cellulose chains either in the C1 or in the C4 ends by the utilization of protein in every case, into the cellobiose units.

Several enzymes, like hemicellulase, pectinase, xylanase, and cellulase, have been used to eliminate the non-cellulosic components. The proposed constituents of the enzyme are a mixture of various proportions of pectinase, hemicellulase, and cellu-

lose [124]. It is well understood that the cellulase enzyme is used to hydrolyze the cellulose which leads to the removal of amorphous regions.

In recent times, Novozyme presented Scourzyme L to commercialize in the market for the application in textile industry. The enzyme, called pectate lyase, particularly catalyzes the breakdown of internal a-1,4-glycosidic linkages by β removal in pectic acid (pectate) at alkaline pH between 8 and 10. The specific attack on carboxylic acids decreases the acid constituent in the natural fibers, giving rise to low hydrophilic characteristics. Generally, this enzymatic method could be well fitted to the cellulosic fibers comprising of pectin.

Enzymatic pectin removal in the traditional softening procedure results in disassembly of fiber bundles in fibrous crops, like hemp and flax [125–127].

6 Biocomposites with Nanocellulose

6.1 Biocomposites Incorporated with Cellulose Nanocrystals

Chen et al. [128] produced nanocomposites with polylactide-grafted CNC (CNC-g-PLA) and poly(bhydroxybutyrate) (PHB) as a matrix. The results suggest that the nanocomposites with unmodified CNC exhibited a greater crystallization rate compared to neat PHB, whereas CNC-gPLA showed less crystallization degree. Additionally, several researchers illustrated that the CNC can also be able to act as nucleating agents, which affect the crystalline degree of the polymer [129, 130].

Fortunati et al. [131] developed poly(lactic acid) (PLA)-based nanocomposite films reinforced with modified CNC with an acid phosphate ester of ethoxylated nonylphenol (Beycostat A B09). The report suggests that the surfactant helps in NC distribution in the polymer composites, augmenting the nucleation effect of CNC and leading to plasticization.

The biocomposites prepared based on various polymers such as PLA [132, 133] and alginate [134] reinforced with CNC have been proven for the enhanced thermal properties of biocomposites. Starch biocomposite film with the addition of CNC content could increase the crystallinity up to 15% CNC [135].

Azeredo et al. [136] investigated the influence of CNC extracted from cotton or coconut husk fiber on alginate–acerola film. The biocomposite reinforced with CNC from both the fibers exhibited similar tensile and water vapor permeability. Similarly, Azeredo et al. [137] examined the effect of CNC isolated from coconut fiber on alginate-based film and compared with the nanoclay as a reinforcing agent. Both the biocomposite film showed better water vapor permeability than the pure matrix film.

A bio-nanocomposite film based on PLA reinforced with CNC at a concentration of 1wt% and 5 wt% results in improved tensile properties as well as transparency [138]. Likewise, the water vapor permeability was enhanced when the modified CNC and different concentrations of pristine were added to PLA [139]. A nanocomposite

film prepared by using chitosan, CNC, glycerol, and olive oil exhibited enhanced water resistance and water vapor permeability [140].

6.2 Biocomposites Containing Cellulose Nanofibers

The chitosan [141] and PVA [142] film added with CNF were reported to have improved the thermal properties, water solubility, and water permeability. PLA reinforced with CNF obtained by Iwatake et al. [143] confirms the increased tensile strength and modulus. Similarly, Fernandes et al. [141] obtained the chitosan film with CNF reinforcement which results in the increment of tensile strength and modulus of the composite films. The xylan-rich hemicellulose film prepared with the addition of sorbitol as plasticizer improved the tensile strength and young modulus very effectively [144]. Bilbao-Sainz et al. [145] demonstrated the addition of CNF and TEMPO-CNF to HPMC films and compared it with the HPMC films reinforced with CNC. The results revealed that HPMC with CNC exhibited a better tensile and water vapor barrier properties and good transparency level of the film.

6.3 Biocomposites Reinforced with Bacterial Cellulose

George et al. [146] prepared the PVA-based film reinforced with the 4 wt% BCNC which improved the tensile and thermal properties of the films than the PVA matrix. Moreover, the starch film added with BCNF (50 wt%) exhibited a better tensile strength and modulus [147].

Barud et al. [148] studied the poly(3-hydroxybutyrate) film with bacterial cellulose which results in very good tensile and modulus properties because of its strong interfacial interactions between the BC and PHB networks. Conversely, the chitosan film was developed by Lin et al. [149] and reinforced with BC followed by comparison with the pure BC matrix which confirmed the enhancement of mechanical properties of the biocomposites. Likewise, the gelatin film combined with BC demonstrated the improvement of tensile behavior by interlinking the networks uniformly [55].

7 Development of Nanocellulose-Based Biocomposites

Nanocellulose materials can be produced by different methods which directly enhance the characteristics of final products. The important research efforts are focused on the production of NC-based biodegradable composites with enhanced properties [150].

The incorporation of CNC as reinforcing filler in polymer composites might lead to the formation of H-bonded three-dimensional network within the matrix [151]. This

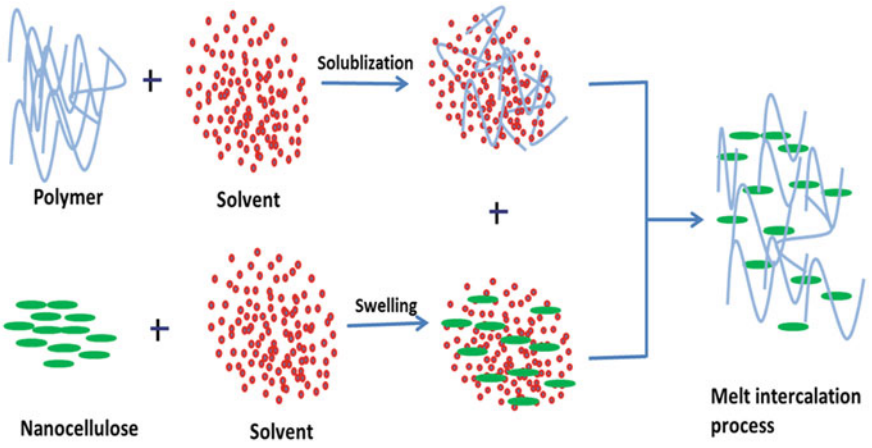

Fig. 5 Melt intercalation processing for the preparation of the bio-nanocomposite film [177]

network gives the energy to withstand the external strains, enhancing the mechanical behavior of nano-biocomposites. Furthermore, the CNC network had good oxygen permeability and improved the thermal behavior of nanocomposites [139]. CNC could also change the crystallization kinetics of the polymer matrices, and also, the surface modification has an important role in this process [152].

Petroleum-based polymers prevail in food packaging because of its simple handling, low cost, and good barrier behavior [153]. The utilization of nanocellulose might prolong the keeping quality of food and may also enhance the quality of food as they could aid as carriers for antimicrobial and antioxidants compounds.

Recently, the fast development of polymeric science and broad utilization of polymeric materials in technology have led to gaining interest in the development and characterization of polymer-based composite (Table 2).

7.1 Melt Processing

The knowledge of using heat to make soften and mold polymers has existed since 1868. John W. Hyatt manufactured a machine for the production of the billiard ball from plastics which can be utilized for the injection of the molten material into a mold form. More than 70 years later, a screw was added to a similar machine, permitting the mixing and recycling of polymers at high temperatures. Melt processing of biocomposites is an important method to market composite materials in large volume, and also, it is very cost-effective and quick progress method (Fig. 5).

Abundant progress has occurred in current techniques for preparing polymeric nanocomposites. The main part of these studies on cellulose nanocomposites is done in liquid media since the materials can reach good or reasonable suspension states

Table 2 Polymer matrix reinforced with nanocellulose to obtain bio-nanocomposite films

Preparation technique	Cellulose source	Biocomposite matrix	Nanocellulose form	CNC (wt%)	References
Solvent casting	Kiwi pruning stalks	PVA_CH/CNC, carvacrol	CNC	3 wt%	Luzi et al. [72]
Solvent casting	Sugarcane bagasse	CMC/ST/CNC	CNC	0.5–5 wt%	Miri et al. [154]
Solvent casting	Barley straw and husk	PVA/CH/CNC	CNC	1–3 wt%	Fortunati et al. [70]
Solvent casting	Red algae	PVA/CNC	CNC	1–8 wt%	Achaby et al. [27]
Solvent casting	Industrial waste cotton	PVA/CNC	CNC	5 wt%	Thambiraj and Ravi Shankaran [69]
Solvent casting	Sugarcane bagasse	PVA/CMC/CNC	CNC	0.5–10 wt%	Achaby et al. [42]
Casting/evaporation technique	Sugarcane bagasse	PVA/CS/CNC	CNC	0.5–5 wt%	Miri et al. [23]
Casting technique	–	CS/CNF	CNF	0–20 wt%	Azeredo et al. [50]
Casting technique	–	CS/NFC	NFC	50%	Fernandes et al. [141]
Casting technique	–	CS/NFC	NFC	32 wt%	Wu et al. [155]
Solvent casting	Softwood kraft pulp	CS/CNW	CNW	5 wt%	Khan et al. [156]
Evaporation technique	Cotton linter	CS/CNW	CNW	0–20 wt%	Li et al. [157]
–	–	CS/CNW	CNW	0.18%	Dehnad et al. [158]
Solvent casting	Rice straw	PVA/CS/CNC	CNC	1–5 wt%	Anand babu et al. [88]
Solution casting	Cotton wool	PVA/CNC	CNC	5–15%	Popescu [89]
Solution casting	Kenaf fibers	TPCS/CNC	CNC	2–10 wt%	Zainuddin et al. [67]
Solution casting	MCC	Sodium caseinate films	CNC	1–3 wt%	Pereda et al. [159]
Solution casting	Wheat straw	Thermoplastic starch/CNF	CNF	–	Alemdar and Sain [57]
Twin-screw extrusion	Kenaf pulp	PLA/CNF	CNF	1–5 wt%	Jonoobi et al. [160]

(continued)

Table 2 (continued)

Preparation technique	Cellulose source	Biocomposite matrix	Nanocellulose form	CNC (wt%)	References
Solution casting	–	NC-MC	NC	0.1–1%	Khan et al. [161]
Compression molding	–	Polycaprolactone + MC matrix/NCC	NCC	7.7%	Boumail et al. [162]
Melt extrusion method	–	PLA/CNW	CNW	–	Oksman et al. [132]
Solution casting	MCC	Alginate biopolymer	CNC	1–10 wt%	Abdollahi et al. [163]
Solution casting	Softwood kraft pulp	Alginate biocomposite	CNC	1–8 wt%	Huq et al. [134]
Compression molding	Needle-leaf bleached kraft pulp	PLA/CNF	CNF	10 wt%	Iwatake et al. [143]
Film casting	Jute and bacterial cellulose	ST/BCNF	BCNF	50 wt% BCNF	Soykeabkaew et al. [147]
Solution casting	Bleached sisal pulp	Xylan-rich hemicellulose films	CNF	20 wt% CNF	Peng et al. [144]
Solution casting	Bleached dry lap eucalyptus pulp	Polyethylene oxide matrix	CNF,CNC	10 wt%	Xu et al. [164]
Solution casting	Softwood pulp	Amylopectin films	CNF	0–10 wt%	López-Rubio et al. [165]
Film casting	–	HPMC films/MCC	CNF, TEMPO-oxidized CNF and CNC	0.08–0.8%	Bilbao-Sainz et al. [145]
Solution casting	*Gluconacetobacter xylinus*	Hydroxypropyl methylcellulose (HPMC)/CNC	BCNC	2 and 4 wt%	George et al. [166]
Heating	–	PVA/CNC	CNC	10%	Paralikar et al. [167]
Solution casting	*Gluconacetobacter xylinus*	Gelatin/BCNC	BCNC	1–5 wt%	George and Siddaramaiah [99]

(continued)

Table 2 (continued)

Preparation technique	Cellulose source	Biocomposite matrix	Nanocellulose form	CNC (wt%)	References
Film casting/evaporation technique	*Luffa cylindrica*	Poly(-caprolactone) (PCL)/CNC	CNC	0–12 wt%	Follain et al. [168]
Solvent exchange cum solution casting technique	Bamboo (Bambu sabalcooa)	Poly(3-hydroxybutyrate)/CNC	CNC	2 wt%	Dhar et al. [169]
Compression molding	Cotton linter pulp	Soy protein isolate	CNC	0–30 wt%	Wang et al. [170]
Solution casting	Pea hull fiber	Starch/CNC	CNC	30 wt%	Chen et al. [171]
Solution casting	Potato (*Solanum tuberosum* L.) tuber	Starch/CMF	CMF	3.3 wt%	Dufresne et al. [172]
Solution casting	*Acetobacter xylinum (G. xylinus)*	PVA/BCNC	BCNC	4 wt%	George et al. [146]
Sulfuric acid hydrolysis	Cotton fiber or coconut husk fiber	Alginate–acerola puree films	CNW	0–15%	Azeredo et al. [136]
Twin-screw microextruder	*Phormium tenax*leaves	PLA/CNC	CNC	1 and 3 wt%	Fortunati et al. [131, 138]
Casting technique	Commercial cotton paper	CS/CNC	CNC	1–12 wt%	Pereda et al. [140]
Solution casting	Eucalyptus wood pulp	CS/CNC	CNC	0–60 wt%	Mesquita et al. [173]
Film casting	–	Mango puree-based edible films	CNC	1–36 g/100 g	Azeredo et al. [174]
In situ chemical polymerization	Wood	TEMPO-oxidized CNF/PVA and PPy	CNF	2.5%	Bideau et al. [175]
Solution casting	Sunflower stalks	CNF and CNC/Gelatin biocomposite	CNF and CNC	0.47–1.46% v/v	Fortunati et al. [101]
Compression molding	Softwood kraft pulp	PCL/NCC	NCC	5 wt%	Khan et al. [176]

in aqueous media and some organic solvents. Nowadays, melt processing method is a greener approach because no solvents are used. Conversely, it involves some complications due to the inconsistencies between cellulose and polymeric matrices. In such cases, the auxiliary method could be followed to produce cellulose-based nanocomposites. Composites prepared by an extrusion technique, injection, in situ polymerization and resin transfer molding are generally found in the literature.

Zhang et al. [178] developed CNC/PBAT nanocomposites with 0.5, 1.0, 1.5, and 2.0 wt% of sulfonated CNC by melt mixing methods and altered by acetic anhydride. They noted that the surface alteration leads to even diffusion and a better interfacial linkage between modified CNC and PBAT, augmenting the mechanical behavior of the nanocomposites. Morelli et al. [179] added CNC produced by acid hydrolysis and altered with phenylbutyl isocyanate in PBAT matrices by melt extrusion technique. The results revealed that the nanocomposites with modified NC exhibited a modulus which was smaller than the modulus of nanocomposites with unmodified NC with the same concentration of nanofillers. They ascribed this result to the greater crystallinity noted in the nanocomposites reinforced with unmodified CNC.

Habibi et al. [180] studied the CNC-g-PDLA added in PLLA matrix by melt processing. They described that the greater mechanical properties are possible because of the stereo complexion that hardens and stabilizes the percolation network.

Castro et al. [181] reported the reinforcement of high-density biopolyethylene with CNW isolated from curauá fiber and castor oil, soy, and linseed epoxidized as compatibilizers. The total process includes the extrusion and hot pressing, targeting to estimate the dispersal of CNW in the polymeric matrix. The TGA/DTG was performed to analyze the thermal degradation of the film incorporated with CNW. Menezes et al. [182] reported the reinforcement of polyethylene with CNW by extrusion technique to produce a nanocomposite film. This research suggests the possibility of CNC processing by a totally industrial procedure without affecting the characteristics desired for the material.

7.2 Injection Molding

It is a technique used to prepare a material with various structures and properties by the combination of different polymers and also by the addition of nanofillers. The injection molding process is well documented for the production of various composites reinforced with nanofibers. In this technique, the polymers are heated to prepare a composite in a definite shape using the mold which results in composites with better crystallization due to the heat transfer into the polymers. The polypropylene composite with CNC was developed by Yousefian and Rodrigue [183] by this injection molding which resulted in the composites with enhanced viscosity.

7.3 Extrusion

Extrusion method is the simplest technique used to prepare the composites based on various polymers including cellulose. This technique is used most commonly due to its easy procedure, and also, it can be useful in the industrial sector. In this method, the dispersion of the particles or agents in the polymer materials is achieved by imposing the mechanical stress through the screw. Alloin et al. [184] developed the nanocomposite films by various techniques including extrusion and casting evaporation for comparison which has proven the significant differences between similar composites. The mechanical properties of similar composites prepared using extrusion method are higher than the casting and evaporation technique at the same concentration of the materials.

Several researchers have reported that the twin-screw extrusion was used to combine the nanocellulose and different polymers such as PP [183], PE [185], and PVA [186]. Moreover, cellulose-based composites result in poor dispersion, while the extrusion method is performing due to the insufficient stress during this process to disperse the materials within the matrix. The dispersion capacity of CNF in the PE matrix was confirmed by using fluorescent marker by Zammarano et al. [187], who used the microscopic technique to identify the dispersion level. In this extrusion technique, the size of the nanofibers is decreased by the shear force which results in better reinforcement leading to strong mechanical properties.

7.4 Resin Transfer Molding

Resin transfer molding or liquid transfer molding is same like injection molding in few aspects. Nevertheless, the classical approach of this method needs prior placing of the filler within the mold in which resin is placed at a lower pressure. In addition, the resin is usually cured after settlement [188]. The process has several advantages like low cost and the possibility of controlling fiber orientation. The first attempt made to prepare nanocomposites by RTM was done by Lekakou et al. [189]. In this work, they suspended nanosilica materials in an appropriate solvent and formed a class of epoxy–silica masterbatch, which was used to produce solid layers. These layers were compacted into glass fabric–epoxy laminates with enhanced mechanical behavior. BC was used as auxiliary filler in thermoplastic composites prepared by liquid transfer molding where sisal fibers were used as continuous fibers [190]. Few researchers utilized NC itself as the mold for the resin. In this procedure, CNF was used as scaffolding for the resin by dipping the dry nanofibers into a resin bath under vacuum. The curing of the resin produced solid particles that were consequently molded by abrasion or pressure [191]. In recent times, Barari et al. [192] examined the influence of modified CNF as a scaffold for resin before curing. The utilization of non-modified cellulose could avoid the diffusion of resin to the middle of the specimen, forming dry spots within the fibrillar structure. The silylation of the CNF

enhanced the spreading of the resin and improved the mechanical response of the post-cure structure than the pristine nanofibers. The alteration step also enhanced the curing of the resin by decreasing its activation energy [193].

7.5 *In Situ Polymerization*

In situ polymerization was the first technique used to develop nanocomposites. Recently, this method was used to prepare the thermoset composites. For thermosets like epoxies or unsaturated polyesters, a curing agent or peroxide is mixed to start the polymerization. For thermoplastics, the polymerization could be started either by the incorporation of a curing agent or by improving the temperature.

The monomer polymerization in the presence of nanofillers is an effective substitute for simply mixing to dispersing the particles in the matrix. The basic knowledge of using in situ polymerization has been applied to the development of cellulose-based nanocomposites (Fig. 6). Polymerization is usually achieved using a sufficient solvent in which the monomers are soluble and the cellulose nanoparticles are dispersible that can include a previous step of drying [194].

As discussed by Iyer and Torkelson [195], these necessities for the solvent could limit the industrial applications of in situ polymerization, as with casting and evaporation techniques. Certain limitations exist on the quantity of nanofiller which can be efficiently dispersed by this method. Auad et al. [196] observed that CNC materials altered by in situ polymerization exhibited higher percolation thresholds compared to non-modified CNC. A moderate addition of CNF could sustain good dispersion during polymerization. Concurrently, the existence of nanofiller altered the viscosity of the system, demanding increased reaction time to finish the polymerization [197]. The rise in viscosity might happen by the surface grafting of cellulose during polymerization method. Rueda et al. [198] explained the use of CNC as precursors of PU chains by grafting 1,6-hexamethylene diisocyanate onto CNC surfaces. The

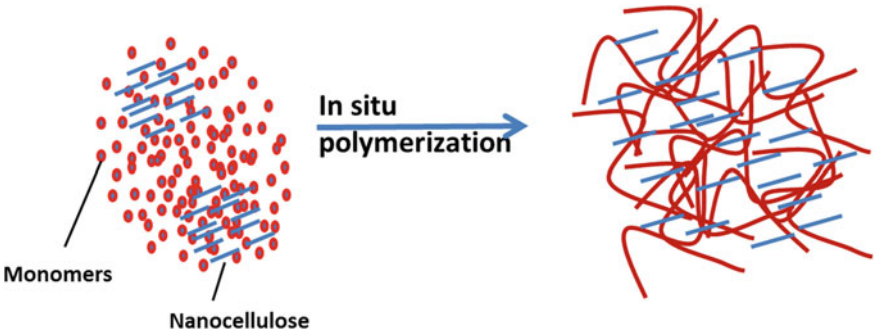

Fig. 6 In situ polymerization for the preparation of bio-nanocomposite film [177]

modified particles were used as templates to produce polymeric chains in a second reaction. A similar method was examined by Yu et al. [199]. The results enhanced the mechanical characteristics of methyl methacrylate (MMA) and butyl acrylate (BA) co-polymer P(MMA-co-BA) using a combination of grafted CNCs with the linear MMA-co-BA. The addition of CNC enhanced Young's modulus and tensile strength of the composite by augmenting the compatibility and entanglement of chain between grafted CNCs and co-polymer. Other properties might also be improved by in situ polymerizations. Müller et al. [200] revealed that the use of bacterial NC permitted the production of membranes with good flexibility for the application in organic electronics. Kaboorani et al. [201] added 1 and 3 wt% of CNC to develop a UV-curable coating for wood furniture. At higher content (e.g., >50%), the hydroxyl groups of NC could be used as crosslinkers for epoxy resins as the nanoparticles self-organize, which produces the iridescent colors and particles with exciting photonic applications [202]. Numerous reports using in situ radical polymerization have been reported previously for the development of nanocomposites based on NC with epoxy resin [203], enzymes [204], hydroxylbutyl acrylate [205], polyamide-6 (PA-6) [206], poly(3,4-ethylenedioxythiophene) [200], poly(n-butyl acrylate-co-methyl methacrylate) [194], poly(*N*-isopropylacrylamide) [207], and among others.

Morelli et al. [208] studied that the sulfonated CNC was grafted using a low molecular weight poly(butylene glutarate) by in situ polymerization method and added the modified nanocellulose into PBAT matrices by the technique of melt extrusion. The grafting improved the thermal behavior of the NC by 208 °C and lessens its hydrophilicity. The addition of 10 wt% of NC augments the tensile and elastic modulus of PBAT around 50%, without modifying its good extensibility and upsurges its storage modulus by almost 200%.

Biocomposite with bacterial cellulose (BC) and polypyrrole (PPy) was produced by Muller et al. [209] using an in situ oxidative polymerization of pyrrole (Py) in the presence of bacterial cellulose hydrogels with ammonium persulfate (APS) as an oxidant. The electrical conductivity, morphology, mechanical behavior, and thermal response of the nanocomposites achieved by ammonium persulfate (BC/PPy·APS) were examined and compared with BC/PPy composites obtained using as oxidant agent Iron III chloride hexahydrate. The morphology, electrical conductivity, and the thermal and mechanical response of/PPy·APS composites were studied and also compared with BC/PPy·$FeCl_3$ composites. The BC/PPy·$FeCl_3$ exhibits the electrical conductivity in the range of 0.01–1.2 S cm^{-1}, i.e., 100-fold higher than the BC/PPy APS composites.

7.6 Layer-by-Layer Lamination

Hand laminating, or layer-by-layer (LbL) laminating, is a simple and easy technique for molding the products by intercalating the layers, either by hand or by spray. The resultant materials are laminated, and the mixture of layer properties could provide the superior surface and mechanical behavior. It is well documented that the desired

properties for various LbL systems are strongly reliant on the number of layers, pH, ionic strength, deposition conditions, and polymerization degree of the materials [210]. When the structure of the layered films of CNC and xyloglucan (XG) was compared to that of films prepared from a direct combination of CNC/XG in water, both resulted in similar thicknesses, however dissimilar in internal structures [211]. LbL normally uses aqueous media to dissolve the alternative layers of oppositely charged molecules.

The application of nanoparticle layers might be used to prepare materials with different characteristics. These layers might act as reinforcing agents or oxygen barriers, or develop materials with biomedical applications, like tablets with outstanding properties as drug carriers [212, 213].

The deposition of CNC from an anisotropic aqueous dispersion is entropy-driven. The materials produce layers with either random or aligned arrangements. The difference in arrangements is achieved by regulating the critical concentration that is dependent on the materials aspect ratio and dispersion of ionic strength [214].

Cranston et al. [215] studied Young's modulus of multilayer films of CNF and polyethyleneimine. The results confirmed that the humidity was vital to the film properties, as the presence of water altered the interlayer interactions, which leads to reductions in the modulus by more than 10 times. Furthermore, the introduction of charged particles like CNC looks like to make difficulties in the layer interactions more than it did for uncharged layered particles. Since layers are usually charged, the particle interface acts as a composite material and interacts particularly with the opposing layer.

Mesquita et al. [216] evaluated the charge properties to generate electrostatic interactions between negatively charged sulfate groups on CNC surfaces and the ammonium groups of chitosan. The prepared films exhibited thick and uniform dispersals of the CNC nanoparticles, with bilayer resulting in an average thickness of 7 nm. At the same time, the average thickness of collagen–CNC system determined was 8.6 nm for bilayers [217].

7.7 Solvent Casting Method

Solvent casting method is one of the easiest techniques for the development of polymer nanocomposites (Fig. 7) as it requires simple apparatus and is less time-consuming; however, in this technique, it is very difficult to manufacture films without sandwiching with another polymer film for support. Additionally, because of its rigidity, the film developed cracks easily, and this leads to easy peeling off into thin layers like mica. Films formed by the extrusion technique and tubular procedure, where the liquid-crystalline polymer (LCP) is considerably melted give rise to the problem of vertical anisotropy and interlayer peeling due to the peculiar alignment features. So, in such cases, if the solvent casting technique is used where, after dissolution in a solvent, the solvent is removed to obtain the product, a non-anisotropic film may be produced and the film could be prepared without melting the LCP. There-

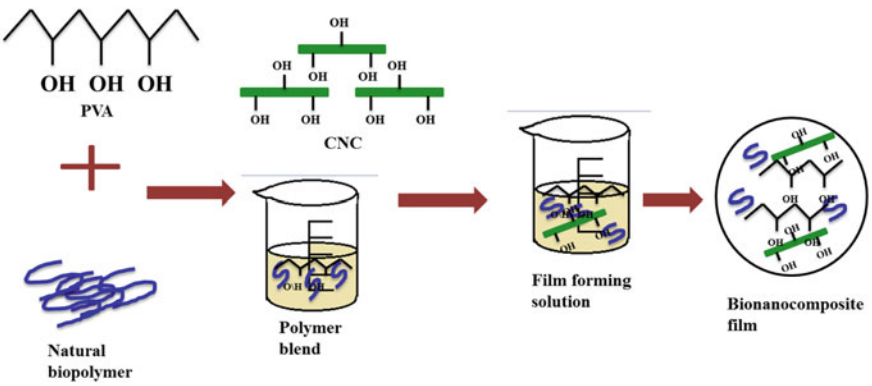

Fig. 7 Preparation of bio-nanocomposite film

fore, solvent-casted films from LCP transfer from an amorphous state to the film by treatment in such a way that the anisotropy in the processing of LCP films does not happen.

Composites produced by casting and evaporation technique result in the maximum mechanical reinforcement presented by CNCs. This is because sample preparation takes place over long time periods. During preparation, the materials have sufficient period to self-assemble into network systems. This method was widely examined in the last 20 years, leading to a well-developed theory and describing the complete potential of cellulose nanoparticles as agents of mechanical reinforcement [183, 218–220].

Nanocomposites might be produced by casting and evaporation technique with the help of polymers matrix which does not need to be water-soluble. A limited number of water-soluble polymers could be directly added with aqueous suspensions of cellulose nanoparticles. This confirms an optimal dispersal of nanoparticles after solvent evaporation technique, while the polymer is dried under controlled conditions. The preferred shape and thickness of the film might also be prepared. Conversely, as with masterbatch production, the use of high-speed homogenizer during polymer dispersion may cause chain scission. Bossard et al. [221] observed a decrease in poly(ethylene oxide) molecular weight led by chain scission during dissolution with stirring at high speed.

Even with these restrictions, the casting technique might be used to prepare very interesting composites. Recently, Cheng et al. [222] used (TEMPO)-oxidized CNF (TOCNF) to prepare waterborne polyurethane coatings (WPU) for the wood application. The addition of various fractions of TOCNF to the polymer–additive mixture intensely enhanced the mechanical behavior of the films. Young's modulus of the film upsurged from 8.6 MPa (pristine WPU) to 440 MPa (5 wt% TOCNF). On the other hand, the inclusion of the nanoparticles also improved the surface roughness of the films from 3 to 27 nm and reduced the adhesive strength of the coating. This reduction was early described by Poaty et al. [223], who described the use of low

molecular weight resins and various ratios of NC to regulate adhesiveness. Other features, like enhanced scratch behavior, have also been defined in the literature [224].

Morelli et al. [208] developed nanocomposites by solvent casting method from PBAT and CNC. Sulfonated CNCs were altered by 4-phenylbutyl isocyanate (5 and 10 wt% of CNC). The results suggest that augmented mechanical response of the nanocomposite with modified CNC to the p–p interfaces between the phenyl rings grafted onto the CNC particles and the aromatic rings of the polymeric chain. Furthermore, the DSC results confirmed that neither the NC incorporation nor their surface modification leads to the lessening of the PBAT amorphous region and in the entire crystallinity of the PBAT matrices.

Gardebjer et al. [225] prepared nanocomposite till 20 wt% of desulfated CNC and chemically altered with PLA. The modified CNC and unmodified CNC were added as nanofillers in three different biodegradable matrices: PLA (polylactide acid), PLGA (poly(lactide-coglycolide)), and PHB by solvent casting technique. The modified NC exhibited low agglomeration and improved interfaces with the polymers like PLA, PLGA, and PHB which are hydrophobic.

Bio-nanocomposites prepared using wheat straw nanofibers and thermoplastic starch (modified potato starch) by solution casting technique [57]. Tensile strength and Young's modulus of the biocomposite films were considerably improved that might be described by the even dispersion of CNF in the polymer matrices. Azeredo et al. [50] prepared chitosan films reinforced with NC and glycerol content as a plasticizer. Sodium caseinate-based films were produced by Pereda et al. [159] with the addition of NC by diffusing the fibers into the film forming solutions, casting, and drying. The composite films exhibited less transparency and more hydrophilic surface when compared to neat sodium caseinate films. Caseinate films developed showed an initial upsurge in the water vapor permeability and then reduced as the filler concentration improved.

7.8 Electrospinning

Electrospinning process produces a nanofiber of films with uniform diameters from the polymer solution with the help of high electric current. The fibers combined with the various polymers will stretch by the electrostatic repulsion between the solvent and surface area which results in nanofibers or films. Two different types of electrospinning methods are generally followed: (1) Two different polymer solution was injected simultaneously through the syringe needle for the formation of nanofibers or films; (2) initially, two polymers are mixed, and the blend was injected into the chamber for the formation of the films which is the most commonly used method for the better achievement of the products with good properties.

Several studies were reported on the electrospinning of the polymers with nanocellulose as reinforcing agents. Zhou et al. [226] stated the nanocellulose-based polyethylene oxide film by electrospinning technique. The rod-like CNC which was

well dispersed in the composite nanofibers by this electrospinning results in the improved mechanical and thermal properties of the composites. The PVA-based nanocomposite films were obtained by Peresin et al. [227, 228] by using the electrospun method. The incorporation of CNC to the polymer composites enhanced the mechanical properties due to the formation of the percolation network by the strong bond fromations [227–229].

8 Nanocellulose-Reinforced Biocomposite in Food Packaging Applications

Chitosan-based films have been effectively used as a packaging material for the preservation of food quality [230]. NC-reinforced nanocomposite films might have a promising effect in food packaging applications in upcoming years because of its excellent mechanical and barrier response. Boumail et al. [162] prepared antimicrobial dispersed films for food applications. Antimicrobial dispersed films demonstrated the maximum tensile strength during storage. In addition, Savadekar et al. [90] productively isolated NFC from short cotton fibers by chemo-mechanical technique.

Abdollahi et al. [163] prepared a bio-based nanocomposite by the addition of cellulose nanoparticles extracted from sulfuric acid hydrolysis into alginate biopolymer by solution casting method. The tensile strength of the biocomposite films augmented with growing NC concentration from 0 to 5 wt%; then, it reduced with an additional upsurge of the filler concentration.

An innovative, technical, and economical process to mix the vermiculite nanoplatelets with NC fiber dispersals into functional biohybrid composites was obtained by Aulin et al. [231]. NC fibers of 20 nm in diameters and several micrometers in length were combined with high aspect ratio exfoliated vermiculite nanoplatelets by high-pressure homogenization.

The influence of CNF in the PLA matrix was demonstrated by Jonoobi et al. [160] in terms of mechanical and dynamic mechanical response in concern of the proposed application in food packaging. The upsurge in tensile strength, Young's modulus, and enhanced visco-elastic behavior were noted for nanocomposites films with 5 wt% of CNF. This highlights the success of the melt component process to produce the cellulose nanocomposites.

All cellulose nanocomposite films were prepared from sugarcane bagasse nanofibers using *N*,*N*-dimethylacetamide/lithium chloride solvent. The research investigated that a very less value agricultural residue could be changed into a high-performance nanocomposite. Cellulose nanocomposite films might be taken as a multiperformance particle with high potential in cellulose-based food packaging application due to its valuable properties such as toughness, bio-based, biodegradability, and acceptable levels of WVP. Thus, cellulose nanocomposite films have the potential for the production of the barrier and protective film in food packaging

industries. The tensile behavior of cellulose nanocomposite films is at least similar to that of other biodegradable or non-biodegradable film [232].

Mechanical behavior of bio-nanocomposites films holding 6 wt% of CNC in thermoplastic cassava starch exhibited the maximum tensile strength of 8.2 MPa. This confirms the stress transfer and interfacial interactions between the matrix and the nanofiller that is associated with the great L/D and effectiveness of the fiber treatment. The kenaf fibers are also noted to be well suited with agar and starch prepared from potato, and the films were evaluated for their potential use in food packaging [233, 234].

An edible film based on alginate–acerola puree reinforced with CNW or MMT of coating application on fresh acerolas minimized fruit weight loss, reduced diseases incidence, and ripening behavior as well as enhanced the retention of ascorbic acid. Similarly, chitosan-based nanocellulose film studied by Dehnad et al. [158], to prolong the shelf life of meat results in reduced lactic acid bacteria than the nylon film packed samples after 6 days of storage at 25 °C.

PLA-CNC biocomposite film incorporated with oregano essential oil prepared by solvent casting was used for packaging to preserve the vegetables which revealed the retardation of *Listeria monocytogenes* during the storage at 4 °C for 14 days. Likewise, PLA-CNC nanocomposite film prepared with the addition of nisin by compression molding method that revealed the inhibition of *L. monocytogenes* for 14 days in cooked ham pack [235]

Cellulose nanofibrils with calcium carbonate were utilized by coating method for the preservation of blueberries [236]. The quality and shelf life of strawberries were enhanced by coating the fruits with chitosan and nanocellulose. It also helps to retain the bioactive compounds [237]. Similarly, Anand Babu et al. [44] reported that the biocomposite film (PVA-Mt/CNC) reinforced with CNC has prolonged the shelf life of mango cultivars till 19 ± 2 days by delaying the ripening behavior and also maintained the overall fruit quality.

Nanocellulose-based polymer composites also exhibit broad applications in various fields such as coatings for food packaging, water treatment, drug delivery, cosmetics, barrier films, and packaging bag for the preservation of food products. Nanocellulose also acts as natural emulsifying and stabilizing agent and might efficiently substitute the hydrophilic polysaccharides produced from seaweeds, microorganisms and carboxymethylcellulose and vegetable seeds. Nanocellulose exhibits great effects on various food products like salads, foams, soups, sauces, and puddings. Nanocellulose-based composites have wide applications in food packaging because of its competence with petroleum-based synthetic materials. CNC and CNF reinforced composites and its coating application, lessening the oxygen permeability that prolongs the keeping quality of the packaged food products as well as reducing the packaging waste of processed foods.

9 Conclusion

Biocomposites reinforced with CNC or CNF has very good potential to use in food packaging applications by substituting the petroleum-based conventional plastics. Some of the disadvantages of the polymer composites like poor mechanical and water vapor permeability limit their use in various applications specifically in food packaging industry. To improve the mechanical and barrier properties of the composites, the nanocellulose was generally used to reinforce with the polymer which may augment the composites behavior like antimicrobial, antioxidant, and mechanical characteristics. The composites with enhanced properties could be well suited for preserving the fruits, vegetables, and other foods in the food packaging applications. Thus, the nanocellulose-based polymer composites will provide the solution to overcome the problems mainly faced by the food industry.

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Chapter 5
The Use of Chitosan in Food Packaging Applications

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1 Introduction

Recently, there has been an increasing demand for natural materials from renewable resources due to their broad availability, reduced health risk, biodegradability, and low cost. Chitosan (CH) is one such natural material that has undergone widespread research in recent years. Chitin a-(1 → 4)-2-acetamido-2-deoxy-d-glucopyranose units and low amounts of -(1 → 4)-2-amino-2-deoxy-d-glucopyranose residues is the precursor of CH. Chitin is chiefly obtained from marine wastes [1] which are strongly linked to various other materials like proteins and minerals. The chitin is obtained by decalcification achieved through acid treatment, after which deproteination is done by an alkaline treatment. Chitin is acetylated and is not soluble in water. When the degree of N-acetylation (DA) is lesser than 50%, it is known as chitosan (Fig. 1).

Various aspects such as alkali content, incubation time, ratio of alkali to chitin, temperature, and particle size affect the alkaline N-deacetylation of CH and therefore influences the activities of CH. Due to the antimicrobial activity, non-toxicity, biodegradability, and easy availability, CH has been used in numerous fields like biomedical, food, agriculture, packaging industry [2].

In comparison with the rest of bio-based food packaging materials, the use of CH has various advantages such as ability to integrate vitamins or minerals, other natural filler materials, and metals, and it holds good antibacterial activity [3]. Based on these properties, CH-based films are used as packaging material for enhancing

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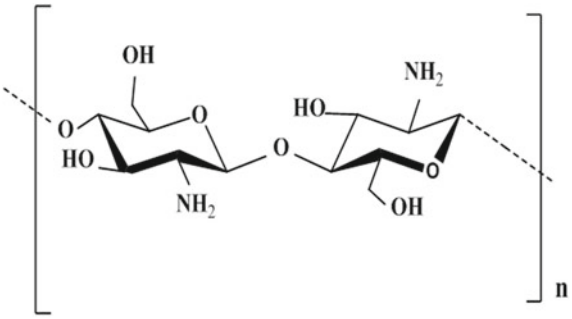

Fig. 1 Chitosan structure

the quality attributes of a number of food products [4, 5]. Hence, in this chapter, we describe the types and preparation of various CH-based films.

2 Chitosan as Packaging Film

2.1 Pure Chitosan-Based Film

Pure CH can be used to make packaging film, mainly as an edible packaging because of its great oxygen and carbon dioxide barrier properties. The environmental-friendly edible CH films were developed mainly to protect foods from spoilage-causing microorganisms and to alter the atmospheres of fresh produce [6]. However, pure CH films are fragile and need plasticizers like glycerol and sorbitol or emulsifiers like Tween-80 which are added to the CH mixture to fabricate films with improved mechanical properties by minimizing the frictional forces among the CH polymer chains, as hydrogen bonds or ionic forces [7]. Various fruits and vegetables such as papaya, tomato, mango could be preserved using CH-based films. Pure CH is dissolved in acid solutions, and films are obtained by solvent casting method [8, 9]. Temperature is the chief factor that influences the physiochemical properties of pure CH film. Leceta et al. [10] demonstrated that the CH film solutions and film showed good antimicrobial properties; however, the bacteriostatic activity reduced with higher temperature (105 °C). Similarly, the functional properties of CH films such as color, and mechanical properties were increased with increasing temperature.

2.2 Chitosan Biopolymer-Based Film

The CH can be combined with various naturally derived biopolymers due to their remarkable properties like non-toxicity, biocompatibility, antimicrobial activity. The developed chitosan/biopolymer films having exceptional characteristics are exten-

sively researched for application in food industry. The biopolymers that are used in combination with CH are polysaccharides, proteins, extracts, organic acids, etc. Thermoplastic corn starch (TPS)- and chitosan oligomers (CO)-based packaging films were prepared to preserve food items like strawberries, ricotta, and flavored bread. The packaging films were prepared by thermocompressing a sandwiched structure containing CO solution between TPS films. The prepared film showed good optical and physical properties. The migration of CO from the film toward the media was determined through diffusion assay. Film sachets were prepared, and strawberries, ricotta, and flavored bread were packed and stored for 7 days. The prepared films showed good antimicrobial activity against molds and yeast. Also, it was observed that the addition of CO into the packaging material showed good microbial suppression than the spraying technique [11].

2.3 Chitosan Synthetic Filler-Based Film

Chitosan film containing synthetic fillers like carbon nanofiber has been fabricated for the manufacture of extremely conductive and resistive materials having superior thermal and mechanical properties. Most of the synthetic filler substances used for making these films are biodegradable in nature, a feature that had permitted researchers to devise substances for biomedical application and as packaging materials. However, the addition of this filler into CH matrix minimizes the natural properties of CH.

2.4 Chitosan Metal-Based Film

Metallic elements like Au and Ag are widely used as fillers for synthetic or natural matrix from ancient times because of their antimicrobial properties [12]. Simultaneously, the ionic interaction between cationic CH and anionic metal nanoparticle has encouraged numerous works which focused on the development of metal- or CH/metal oxide-based composites. Shahzadi et al. [13] developed an amalgam film containing CH and silver nanowires (AgNWs). The addition of 15% of AgNWs increased the tensile strength of the hybrid film. This increase was 62 and 36.7% higher in comparison with the bared CH and CH-AgNPs films, respectively. Notably, resistivity values for the hybrid film were 16 times lower than CH-AgNPs film, suggesting higher conductivity. Also, the film exhibited good inhibition of *E. coli* and *B. subtilis* demonstrating its potential for use in packaging field or medicine.

A CH coating solution containing nanosilicon dioxide was used to preserve harvested jujube which lowered the red index, decay incidence, weight loss, and respiration rate when compared to the uncoated jujube after 32 days. There was a higher antioxidant enzyme activity (i.e., superoxide dismutase, peroxidase, and catalase), total flavonoid content, and lower phenylalanine ammonialyase activity, indicating

that coating jujubes with CH and nanosilicon dioxide may be a promising alternative if nanosilicon dioxide is allowed for food use [14].

2.5 Chitosan Mineral-Based Film

Chitosan biocomposites having mineral filler have been developed to produce coating film with increased toughness and flexibility [15–18]. A CH film-forming solution containing a blend of calcium gluconate and lactate, Gluconal Cal (GC); zinc lactate (5–20%); and R-tocopheryl acetate (5–20%) with acetylated monoglyceride was prepared. The incorporation of GC considerably improved pH and a reduced viscosity of film-forming solutions. The incorporation of higher concentration of mineral or vitamin E in the film matrix improved the water barrier property of the films. The mechanical property of the films was considerably influenced by the addition of GC or VE. Even though a broad endothermic peak at 200 °C was noted in DSC thermograms of CH-based films, only 200% GC addition changed this peak. The investigation established the ability of CH-based film to incorporate an elevated concentration of mineral or vitamin E. These films have application in food packaging such as it can be used for wrapping or coating to improve the nutritional value of foods.

2.6 Chitosan Natural Filler-Based Film

Nanocellulose particles (NCPs) are ideal materials for the synthesis of inexpensive and strong nanocomposites and are more effective filler materials when compared to micro-sized fillers [19]. The NCPs are novel polymer matrices that are having at least one dimension in nanoscale [20], and the chitosan–cellulose-based compounds are of particular interest because of their structural similarity [21]. Khan et al. [22] incorporated 1–10% nanocrystalline cellulose in CH biocomposite improved the mechanical, barrier properties and decreased the water vapour permeability of the films. Chitosan/nanocellulose biocomposites were prepared with 20–50 nm diameter NCPs and different concentrations of 30, 60, and 90% (v/w CH) glycerol. Even distribution of particles in the polymer matrix was achieved by agitation and sonication. The developed film was examined for its thermal behavior, crystalline nature, and antimicrobial activity; also, the film was coated on the ground meat surface to determine its coating ability. Chitosan/nanocellulose nanocomposites showed increased Tg value, and the solid state was intact until the 97–99 °C temperature (Tm). After the addition of CH, nanocellulose peak completely disappeared. The NCPs showed antimicrobial activity (contact inhibition) against both gram-positive (*S. aureus*) and gram-negative (*E. coli* and *S. enteritidis*) bacteria. The comparative study of the application of NCPs on the meat lowered lactic acid bacteria count in comparison with nylon-packaged samples up to 1.3 and 3.1 log values at 3 and 25 °C after 6 days of storage, respectively [23, 24].

2.7 Chitosan Extracts-Based Film

Films containing extracts (active packaging systems) are prepared with the aim of prolonging the keeping quality of fresh produce and meats by preserving the quality attributes. The active packaging system includes physical, chemical, or biological actions which modify interactions among the film, food, or headspace to obtain the preferred results [25]. The most common active packaging systems scavenge the reactive oxygen species from the package or packed product [26]. In an earlier study, the effects of green tea extracts (GTE) and black tea extracts (BTE) on the physical, structural, and radical scavenging activity of CH films indicated that the addition of TE considerably lowered the water vapor permeability and improved the radical scavenging properties of the films. The antioxidant activity of GTE films was higher than that of BTE films in all food simulants (0, 20, 75, and 95% ethanol). The thermal and FTIR spectra analysis suggested that there was a good correlation between film matrices, and this was reflected by the enhanced physical and mechanical activity of composite films [27].

2.8 Chitosan Synthetic Polymer-Based Film

Chitosan has certain drawbacks because CH is not thermoplastic, and it degrades before the melting point. Thus, unlike conventional thermoplastic polymers, CH cannot be extruded or molded and the films cannot be heat-sealed [28]. The blending of CH with thermoplastic polymers, like polyvinyl alcohol, polylactic acid, has proven to be efficient. A blended film from poly(vinyl alcohol) [PVA] containing CH was prepared via solution casting and electrospraying method for food packaging application [29]. The PVA–CH films exhibited greater elongation at break, reduced oxygen permeability, improved water barrier properties, and high antibacterial activity when compared to the pure PVA film, especially for the PVA:CH weight ratio of 75:25.

3 Preparation of Chitosan-Based Films

3.1 Solvent Casting

The solution casting method is the most widely used technique for preparing CH films. The solution casting process involves the dissolution of CH powder in an acidic solution, and later, the solution is poured onto a petri dish, glass plate, plastic plates, etc. The polymer solutions are then dried in room temperature or at a specific temperature in desiccators, hot air oven, convection oven, etc., till the film is entirely dry, and then, it is peeled off from mold (Fig. 2).

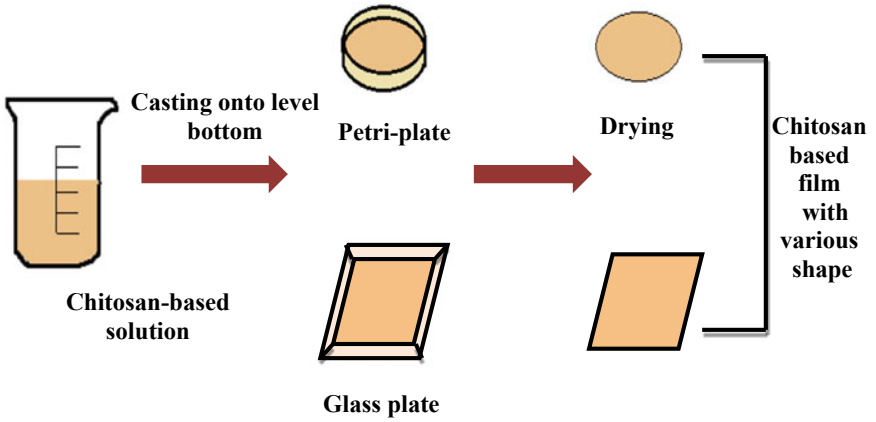

Fig. 2 Solvent casting technique [54]

The CH film formation occurs due to the intermolecular interactions like electrostatic and hydrogen bonding during the drying process. However, such interactions between the chains make the films brittle, and hence, the addition of plasticizers or blending with various other polymers and proteins is necessary to improve their mechanical properties [30]. Several researchers have suggested that the addition of specific materials (e.g., cellulose) to CH-based film has increased the mechanical barrier property of the film and enhanced the food safety, quality, and shelf life of the stored food products [30–32].

3.2 Dipping and Spray Coating

Coatings are chiefly used for developing an edible packaging system. Recently, CH has garnered considerable interest as a suitable edible coating matrix for vegetables and fruits [33, 34]. Edible coating systems help in preserving the food quality and prolong their shelf life. The two important ways to coat a food material are dipping and spray coating. Dipping consists of introducing the food material in the beforehand prepared acidic film-forming solution, while spraying consists of pulverizing the film-forming solution by using an aerosol [10, 35]. In the dip coating method, the product (food samples) is dipped directly into the film-forming/coating solution which leads to the creation of a thin membrane film over the surface of the product, following which it is allowed to air-dry (Fig. 3). The thickness of the film is determined by the density, viscosity, and surface tension of coating solution [36]. Mannozzi et al. [6] showed that dip coating of blueberry with chitosan and chitosan + procyanidin maintained the firmness and enhanced the antioxidant activity (DPPH and ABTS methods) of blueberry. Also, the overall fruit quality was maintained during storage.

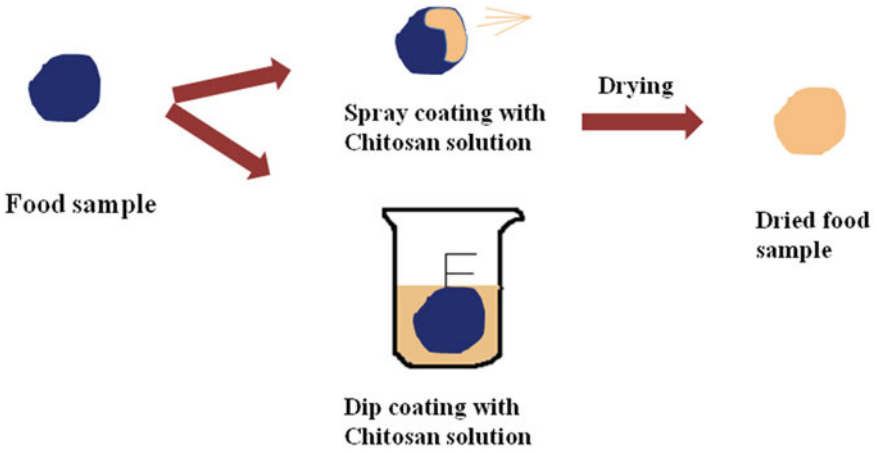

Fig. 3 Dipping and spray coating [54]

For the low-viscosity coating solution, spray coating technique can be used [37, 38]. In the case of the conventional spray coating system, the size of the droplet can be up to 20 μm; however, the electrospraying system makes even sized particles lower than 100 nm from polymer and biopolymer solutions. Factors such as drying time, temperature, method affect the development of polymeric coatings by spraying systems. This is due to the protonation of CS amine groups in acidic media, giving caustic characteristics to CH which reduces some sensorial attributes.

3.3 Layer by Layer

A layer-by-layer (LbL) deposition method has been widely used for preparing layered thin films by a buildup of consecutive layers of oppositely charged species [39–41]. The layer-by-layer method is based on the electrostatic force of attraction, hydrogen bonding, and affinity between synthetic polymers, proteins, polysaccharides, etc. The technique has been used for the fabrication of layered thin films having a range of properties including increased adhesion, elasticity, biocompatibility, mechanical properties, and wettability [42–44]. Chitosan has been used to make LbL-based films and coatings because of its cationic nature [45]. A substrate is required to prepare such films. This substrate is submerged in the CH solution, and a very thin film is formed on the surface. The multifaceted films developed from the LbL assembly of CH with various polymers are well-characterized concerning thickness difference, permeability to gases and glucose, and mechanical and thermal properties [46]. Factors including pH and ionic strength during deposition determine the properties of these films. The post-processing of films includes chemical or ionic cross-linking of components, which may affect the mechanical performance [46].

Previously, Acevedo-Fani et al. [47] demonstrated that LbL-assembled CH/alginate thin coatings help in improving the properties of food including texture and color, to develop active packaging and prolong the shelf life of the food.

3.4 Blending

Chitosan is usually mixed with other polymers by solution blending or extrusion blending which lead to film with better physiochemical properties when compared to the solvent evaporation technique [28].

3.4.1 Solution Blending

Solution blending consists of mixing two or more solutions and developing films by solution casting method. Volpe et al. [48] blended sodium caseinate (SC) and CH in various concentrations to obtain 16 different blend films. All the blend films exhibited increased mechanical property and reduced hydrophilicity when compared to pure CH film, and increasing concentration of CH increased the metastability of the film. Mohammadi et al. [49] reported the synthesis of CH, gelatin, and eggshell-based blend film, and it was suggested that the addition of CH with negatively charged polysaccharides increased the mechanical characteristics and reduced the solubility and water vapor permeability of the gelatin films.

Similar studies by Hu and Wang [50] reported that the films developed by the addition of different amounts of propyl-3-trimethyl ammonium chloride chitosan (HTCC) into polyvinyl alcohol (PVA) matrix improved the tensile strength, transmittance, flexibility and low oxygen permeability of the film. It was observed that the HTCC and PVA had good compatibility and were compatible via the hydrogen bond formation among the hydroxyl groups of HTCC and PVA in the blend films. In comparison with the pure PVA film, the WVP of the hybrid films was enhanced, and also, the developed films exhibited considerable antibacterial activity against *S. aureus* and *E. coli*. The polymer blending is a simple and efficient technique to get new material with desired characteristics [51], and the blend films could be applied in food packaging industry.

3.4.2 Extrusion

Extrusion technology is a commercial process commonly used to fabricate film. The major advantage of extrusion technology is its high productivity and minimal space requirements in comparison with casting method [52]. There are various types of extruding method (Fig. 4), and one such method includes melt extruding, where the developed film usually has good mechanical properties and thermal stability [53]. In the case of two-step melt-compounding process, when the CH concentration increased, the elongation at break reduced and the water vapor permeability

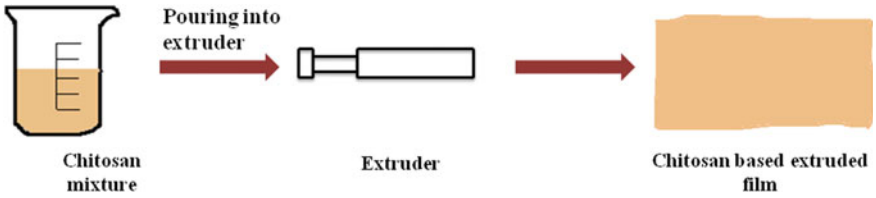

Fig. 4 Extrusion method [56]

was increased. A film based on CH, poly(lactic acid) (PLA), and polyethylene-graft-maleic anhydride was fabricated by extrusion molding [54]. The obtained film had good transparency, and the concentration of low-density polyethylene determined the thermal property of the developed biocomposite. The three-step extrusion processing could extrude films without degradation. The extrusion method is an efficient method to develop films having excellent mechanical and thermal properties, and antimicrobial activity [55]. These blending methods have various advantages in film preparation.

4 Conclusion

The potential of chitosan, as shown by research and development efforts, is supported and improved by increasing consumer demand for natural and safer additives with functional properties and increasing environmental concerns. Chitosan is a natural material which has attractive properties like antimicrobial and film-forming activities. The usage of CH as a coating material, films, and blends would contribute to the preservation of quality attributes of food and extension of shelf life. However, more researches are required to optimize the antimicrobial activity of chitosan films and to understand the influence of various parameters on the antimicrobial activity and accessibility of chitosan.

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Chapter 6
The Use of Biopolymers in Food Packaging

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1 Introduction

The effects of human activities on the environment cannot be overlooked. It is crystal clear from natural science view that human's activities are vandalizing the planet. Climate change is considered as the third most worrying issue facing our World today. The several damages to the planet are results of overuse of natural resources

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by stressing the nature beyond its capacity [1]. From the agricultural perspective, food productions/resources are not evenly distributed across the World, justifying starving of a large population that occurs in the World today [2]. This means foods have to be produced from one area/country and distributed to other parts it needs. No country is 100% independent in terms of total food productions and consumptions. Trade among countries means farm produces have to be well packaged and transported among trade partners with appropriate packaging materials. Annual world plastics production hits over 300 million metric tons [3].

"Packaging is all products that are of any nature and used as the containment, handling, protection, presentation, and delivery of goods from the raw materials state to the processed goods and from the producers to the consumers" [4]. Sometimes materials for packing or the nature of packaging could make a big difference in the way the product is accepted. In recent time, packaging materials have been a serious concern to the environment and it is being thoroughly debated among the stakeholders. Food-packaging materials protect the products from the processing stage up until the usage point by consumers; after which most of the materials are left to the mercies of the environment to decompose them.

Since the 1930s when plastic was invented, it is preferably used in food-packaging industries. Plastics are often used because of their numerous advantages in food packaging some of which include:

(a) Flexibility: Their flexible characteristics enable the manufacturers to produce them in different shapes or sizes according to demands.
(b) Lightweight: This means that plastics can be transported from one place to another in large quantities.
(c) Plastics can withstand the extreme situation of hot or cold weather without seriously affecting the food content. They also protect food against dust, contaminations, reaction to light and moisture.
(d) Low production cost: Plastics' production for food packaging does not require huge sum of the money, making them to be economical for small-scale businesses.

Plastics industries are faced with two crucial problems [5]. The first is the fact that its production solely on petroleum which environmental scientist see as a danger to human and ecosystem. Secondly, waste disposal. The disastrous and deep-rotted effects of plastics in the environment overshadow any of its benefits one can think of [6]. Many researchers are now intensifying efforts to shift away from petroleum because of its destructive effects on our ecosystem. This means all its products including plastics will be soon faced out. It also implies that food-packaging innovation technology must bridge the gap between food safeguarding and other pressing matters like waste disposal, energy, material cost, and environmental impacts. The challenges of disposing massive quantities of wastes generated by non-biodegradable packaging material pave way for the study of biopolymers as alternative materials for food packaging [7]. In addition, the increase in the prices of petrochemicals and the environmental effects, have now the pushed-up material development of natural

polymeric materials for various applications, including food-packaging materials, which are more consumer-friendly.

2 Biopolymers

Natural polymers are regarded as biopolymers and are produced by living organisms. Biopolymers are polymers that are known to be biodegradable. The prefix "bio" indicates that the biopolymers are biodegradable. The word biodegradable indicates that materials can be degraded by the action of enzymatic living organisms, like bacteria, fungi, yeasts, and the final end-products of the biomass under anaerobic conditions, hydrocarbons, and methane [8]. These kinds of polymers consist of monomeric units which are bonded covalently, forming chain-like molecules. Furthermore, they are produced within the cell by the process of complex metabolic. Biopolymers are used as a replacements for oil-based plastic materials made from petroleum. This is due to their biodegradable nature, renewable and they are abundantly available [9].

2.1 Classification of Biopolymers

Biopolymers can be classified generally based on their source:

1. Polymers that are directly removed/extracted from biomass such as polysaccharides (starch, galactomannans, and cellulose) and proteins (gluten and casein).
2. Those that are the product of chemical synthesis made from renewable bio-derived monomers, like polylactic acid (PLA), thermoplastic aliphatic polyester which is derived from lactic acid monomers. Fermentation of carbohydrate feedstocks is the process of producing the monomer.
3. The polymers developed by microorganisms, such as polysaccharides (pullulan and gellan gum) and polyhydroxyalkanoates (PHA) [10, 11].

3 Food Packaging

Packaging is the last stage of the production of agricultural products before they are transported and presented to the market for consumers. Food packaging can be defined as an organized structure of getting the food ready for transportation, distribution, storage, retailing, and end-use for the satisfaction of the consumer at an affordable cost [12]. In other word, packaging can be described as art, science, and technology of preparing products for the market. Food-packaging materials can be made from any material such as aluminum, wood, plastic, glass, or paper. Packaging techniques can be classified into four categories, namely: unit load, tertiary

packaging, secondary packaging, and primary packaging. The properties of food-packaging materials include thermal, mechanical, and optical properties, barrier (i.e., to moisture, carbon dioxide, oxygen, and flavor), and antimicrobial. Containment of bacteria is the main goal of a package. Packaging provides protection of food from spoilage by water, gases, microorganisms, dust, and punctures. A food package tells more information about the product, how to prepare it, and information about the nutritional content.

Food packing should be done in such a way that it will maintain the sensory properties of the product, i.e., color, taste, texture, and aroma. The shape, size, gloss, and vibrant color attract consumers and influence the decision of buying a product [13]. Food packaging is an essential way to increase the shelf life, maintaining the product quality and safety of the packaged products, nevertheless, packaging materials such as plastics can have an adverse effect on the environment because of they are non-biodegradable [14].

4 Biopolymers Used in Food Packaging

The focus currently is finding alternatives for petroleum and reducing the negative environmental impact. Research focus is on the development of biodegradable food-packaging materials from biopolymer-based materials. Biopolymer-based (proteins, lipids, and polysaccharides or the combinations have the ability to replace current synthetic-based plastics [15]. According to Vieira et al. [16], bioplastics account for between 5 and 10% of the available plastics in the market. The natural biopolymers find useful applications in food packaging due to the advantages such as availability of renewing resources, biodegradable, biocompatible; these attributes encourage ecological safety [17]. The origin of biopolymer-based packaging materials is from natural-renewable resources and can be classified based on their general composition. Table 1 shows biodegradable polymers (and their classifications) used in food packaging.

4.1 Polysaccharides

Polysaccharides may be homo-polysaccharides that are made up of a single monosaccharide or hetero-polysaccharides having two or more sugars. Homo-polysaccharides contain linear chains polysaccharides such as pullulan, curdlan, levan, or bacterial cellulose while hetero comprises of multiple copies of oligosaccharides, like xanthan and gellan.

Polysaccharide is the most prolific macromolecule in the biosphere. Complex carbohydrates, which are constituted by glycosidic bonds, are mostly one of the major plant structural elements, for example, cellulose and animal exoskeletons like chitin or have an important role in the plant energy storage such as starch [18].

Table 1 Biodegradable polymers used in food packaging depending on the general chemical composition [89]

Polysaccharides	Proteins	Aliphatic polyesters
Alignate	Collagen	Polylactic acid (PLA)
Carrageenan	Gelatin	Polyhydroxybutyrate (PHB)
Cellulose	Whey protein	
Chitin/Chitosan	Soy protein	
Curdlan	Zein	
Gellan		
Pectin		
Pullulan		
Starch		
Xanthan		

Polysaccharides provide many varieties of glycosidically linked structures which are based on 40 different monosaccharides. Certain material properties like water uptake, biocompatibility, and reinforcing effects have been linked to polyglucoside acrylates. The following are important structural polysaccharides that play a major role in biopolymer production. Polysaccharides are a fundamental part of any living system, being a structural unit or an energy storage unit. The source of polysaccharides can be used to determine which group they belong animal, plant and microbial and living organisms contain different forms of polysaccharides. Polysaccharide is one of the indispensable biomolecules know on earth.

Biopolymers or microbial polysaccharides can be used as gelling agents and/or to alter liquid flow characteristics. Recently, the interest in bacterial polysaccharides has grown and more advanced study of their compositions, structures, biosynthesis, and functions have been reported in literature. Bacterial polysaccharides can be Lipopolysaccharide (LPS) (which is confined to the outer bacterial cell membrane) or capsular polysaccharides (CPS) (which forms a discrete surface layer (capsule) or exopolysaccharides (EPS) which is loosely bound to the surface of the cell. CPS possess functions that are related to the pathogenicity and adherence of bacterial cell, while EPS extends multiple support functions like biofilm formation, adhesion, protection, and cell–cell interaction from the extreme environment. Figure 1 shows the structure of polysaccharide (cellulose) and its hydrogen bonds.

4.1.1 Starch

Starch is frequently used in edible film processing. Amylose and amylopectin provide hydrogen bonding and as a result, starch-based films can be easily dissolved in water and bind with other polar functional groups [19]. Advantages of starch as an edible film include simplicity of preparation, inexpensive, and a good barrier to lipids and oxygen. However, it has poor water resistance. Starch-based edible films can be

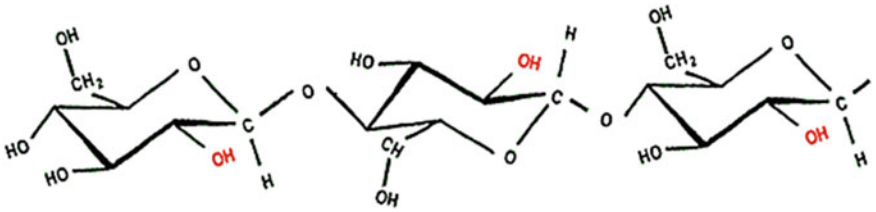

Fig. 1 Structure of polysaccharide (cellulose). *Source* Dynamic science

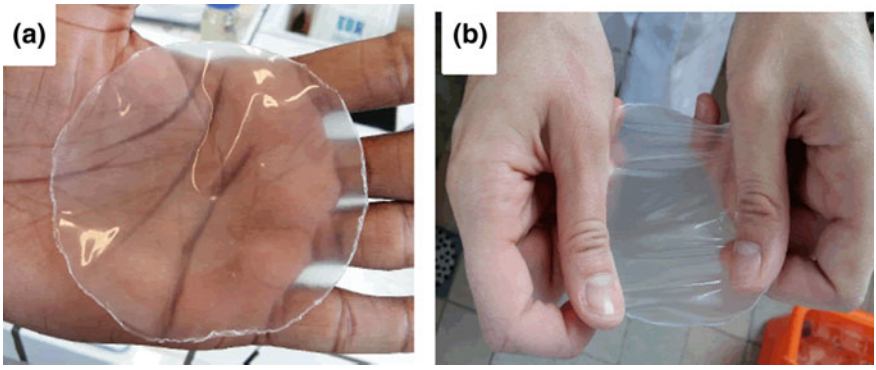

Fig. 2 Cassava starch-based emulsified film **a** appearance of the firm and **b** flexibility of the film. *Source* Adjouman et al. [87]

used to package candy and bakery products [19]. As an example of an application, the sticky surface of candies wrapped with a thin-starch-based film minimizes the inconvenience of the product sticking to a consumer's fingers [20]. The combined plasticizers effect and blends on the starch-based edible film properties showed that films having glycerol and high concentration of surfactant behaved similarly to films having a relatively higher plasticizer content [21].

Starch-based plastic used as a packaging material is excessively brittle. Starch as a standalone lacks the ability to form films possessing expected mechanical properties such as high elongation, tensile strength, and flexural strength, except it is blended with other materials, chemically modified, plasticized, or combination of these treatments. Common plasticizers used include glycerol and other low molecular-weight polyhydroxy-compounds, polyethers, and urea. Figure 2 shows cassava starch-based emulsified films.

4.1.2 Chitin/Chitosan

Chitosan is the second largest polymer after cellulose. Chitosan is a natural polymer extracted from chitin). Chitosan has been observed for many years to possess tough antimicrobial properties against viruses, bacteria, and fungi [22]. However,

there are few drawbacks in terms of mechanical properties; gas and water vapor permeability limit its uses. Chitosan is insoluble in water but very soluble in acid solutions like acetic, citric, and formic acids because of its cationic characteristic. It has been approved for its antimicrobial, biodegradable, biomedical, biocompatible properties and can be used in food- and health-related products [23]. Chitosan is obtainable from shellfish industrial wastes, and for this reason, it is an abundantly available material currently. Chitosan is equally obtainable from the chitin component of fungal cell walls (*Histoplasma farciminosum and Aspergillus fumigates*) and from the yeast *Saccharomyces cerevisiae* [24, 25]. Antimicrobial packaging from chitosan is the packaging system that has the potential to kill or inhibit spoilage and pathogenic microorganisms that contaminate food. Antimicrobial packaging has the ability to extend the shelf life of food, therefore, improving the quality of the packaged food. Chitosan is a promising food-packaging polymer that is biodegradable. Furthermore, chitosan has significant potential as a packaging antimicrobial due to its antimicrobial activity, non-toxicity, and biodegradability leading to a large range of applications. Chitosan film's functional properties can be enhanced when combined with other film-forming materials used for food-packaging technology; this is relentlessly developing an answer to the growing problems from the present society. Chitosan is the second most abundant known polysaccharide found in nature after the likes of cellulose, and it is a deacetylated derivative of chitin.

Chitosan is a non-toxic, biodegradable, and biocompatible, thus, considered as an environmentally friendly material for packaging. Active packaging is an innovative approach to improve the shelf life of food while improving the quality, integrity, and safety. Furthermore, chitosan is a good inhibitor against the growth of a wide range of fungi, bacteria, and yeasts and displays good properties for gas and aroma barrier in dry conditions. In addition to these characteristics, the ease of film formation makes chitosan a good choice for active antimicrobial applications for food packaging. Chitosan and chitin biopolymers have the capability to be useful in the food-packaging industries [26].

4.1.3 Curdlan

Curdlan is a linear polysaccharide that forms compound tertiary structures culminating from intermolecular and intramolecular hydrogen bonding [27, 28]. According to Lo and Ramsden [29], curdlan is also able to form colorless, odorless, and tasteless hydrogel complexes with other polysaccharides. The distinctive gelling mechanism can be used to increase the absorption or retention of moisture and other ingredients [27]; while withstanding the extreme temperatures of freezing and retorting processes [30, 31]. The level of interest in many fields that curdlan has attracted, as biopolymer, is due to its successful usage in the packaging industry, which is linked to its excellent film-forming ability, biodegradability, non-toxicity, and it is relatively available. Curdlan is insoluble in water. The heat-gelling and water-binding functionalities make curdlan very important in the food industries [32]. By the reason of

its great thermal characteristics and water-insoluble, it can improve thermal stability and water barrier capacity of the bilayer and multilayer film-packaging materials.

4.1.4 Cellulose

The most known abundantly occurring natural polymer to humanity is cellulose and—like starch—is also comprised of glucose monomer units. Unlike starch, cellulose glucose units are joined together via β-1,4 glycosidic linkages; this enables packing tightly together of cellulose chains, forming strong inter-chain hydrogen bonds. It has been the focus of research recently to develop cellulose derivatives for use in the packaging applications. According to Rein et al. [33], cellulose molecules have amphiphilic character and possess high density of hydroxyl groups and consist of a chain of β-(1 → 4)-linked glucose residues.

Cellulose is the structural polysaccharide of plants, and it exists in cotton, wood, cereal straw, just to mention a few. Cellulose naturally occurs in a crystalline state. From the cell walls, cellulose is isolated in microfibrils by chemical extraction. In all forms, cellulose is known to be highly crystalline, having high molecular weight, which is insoluble and infusible in all but the most aggressive, hydrogen bond-breaking solvents such as N-methylmorpholine-*N*-oxide. Based on infusibility and insolubility, cellulose is converted into its derivatives to make it more processable. For example, sugarcane pulp fiber without chlorine bleach or ECF is used to make food-packaging materials. The fiber is pounded and steered. Molding of the material can be done both wet and dry with focus hygiene and safety. Since the materials are naturally made from sugarcane fiber, the product is safe for the consumer and can withstand temperatures from −40 to 250 °C. The product can be frozen and can hold boiling water at 100 °C or boiling oil at 150 °C, without leaking.

More importantly, sugarcane pulp fiber is biodegradable by landfill within 45 days. The material can be used in the production of packaging materials, such as: plate, cups, and compartment boxes. Figure 3 shows some food and beverage materials made from sugarcane.

4.1.5 Carrageenan

Carrageenan is hydrophilic naturally, anionic sulfated linear polysaccharide produced from red seaweeds, specifically from the family of *Rhodophyceae* (e.g., *Eucheuma* spp., *Kappaphycus* spp., *Chondruscrispus*, and *Gigartina stellata*) [34]. There exist three main species of carrageenan, i.e., (κ, ι, and λ-carrageenan), the structures of their disaccharide differ. In food industry, κ-carrageenan is the most used [35]. Edible films and coatings are the product of carrageenan. Coatings, edible films, and the blends of carrageenan with different polymers have been reported to be useful in food preservation for freshly cut fruits because it reduces moisture losses, decrease gas exchange, prevent discoloration and maintains the fruit's texture [36]. Films of

Fig. 3 Food and beverage materials, made from sugarcane

carrageenan have equally been reported in the literature as encapsulating matrices of aroma compounds.

4.1.6 Alginate

Alginate is also natural polysaccharide which comprises between 30 and 60% of brown algae (on the basis of dry weight) as a calcium, magnesium, and sodium salts of alginic acid. Calcium alginates are insoluble in water. Alginate has dietary fiber properties. Alginate is a binary copolymer and in each of the constituent residue contains carboxyl groups. The structure is made up of β-D-mannuronic acid monomer that is linked to α-L-guluronic acid monomer, through 1,4-glycoside linkage [37]. From *Azotobacter vinelandii*, bacterial alginate can be extracted [38].

According to Sriamornsak and Kennedy [39], the use of alginate in food industries is common practice in the past for applications such as gelling agent, thickening agent, and colloidal stabilizer. Some of the alginate properties such as biodegradability, low cost, biocompatibility, and non-toxicity make it appealing film compound. Algal purification is the first by-product is sodium alginate, which is widely used in the industry. Having an efficient brown seaweed extraction makes it interesting for the production of environmentally friendly biopolymer extract for several applications in the industries, such as release agents, food-packaging material, paper, pharmaceutical, and medical uses, just to mention a few [40]. Membranes of alginate are

strong due to its linear structure, adequate fibrous structures in its solid state, which has been considered a good filmogenic material [41].

4.1.7 Gellan Gum

Gellan gum is a water-soluble anionic polysaccharide formed by the bacterium. In food industry, gellan gum is normally used as an additive (gelling agent, thickening agent, thickener, and stabilizer) for baked goods, sauces, jams, dairy products, and confectioneries. In the European Union, it is labeled as E number E418 (nutrientsreview.com). Nevertheless, it can also be incorporated into coatings and membranes for the food industry, such as batters and breading for fish, chicken, cheese, potatoes, vegetables, coatings, and adhesion. Gellan gum membranes and coatings have several advantages; they have the capacity to minimize oil absorption through the provision of the effective barrier. In batters, for instance, product crispness is maintained for long after baking or frying, which contributes to maintaining the product quality (nutrientsreview.com).

4.1.8 Pectin

Pectin is an amorphous, white, and colloidal carbohydrate with high molecular weight occurring in ripe fruits, particularly in apples and currants. The presence of pectic substances is found in the primary cell walls and middle lamellae of several fruits and plants, and they are normally associated with the structures of cellulose, hemicellulose, and lignin. Pectin backbone comprises of (1 → 4)-α-D-galacturonic acid molecules linked to a small number of rhamnose residues in the main chain and arabinose, galactose, and xylose in the side chains [42]. Edible coatings produced from pectin and its derivatives such as pectate and amidated pectin have been lately suggested for food-related applications based on their excellent barrier to oxygen, barrier to oil, aroma preservation, and good mechanical properties. The authors further reported the drawback associated with pectin for food-related application to be ineffectiveness against moisture transfer through the films by their hydrophilic nature [43].

Pectin major sources of commercial extraction are apple, pomace, and citrus peels, which are by-products from juice industry [44]. High degree of methoxyl groups are available in the orange peel pectin and hence, it possesses a great gelling power in an aqueous medium due to the presence of polar groups that interact firmly with water molecules, producing viscoelastic solutions. Because of its rheological properties and non-toxicity, pectin is widely used in the food industry as stabilizers, thickeners, texturizers, and emulsifiers. Incorporation of pectin edible films has been carried out with several antimicrobial substances in order to obtain antimicrobial active packaging that enhances product shelf life extension and reduces the risk of pathogen growth on food surfaces. Antimicrobial active packaging is a type of packaging that alters conditions surrounding the food to maintain product quality

by the controlled diffusion of one or more antimicrobial agents from the packaging material to the product [45].

4.1.9 Pullulan

Pullulan is a non-ionic exopolysaccharide, which is produced from the fermentation of the fungus-like yeast. It is a biodegradable polymer with low viscosity that is not distorted by heat, sodium chloride and change in pH [46]. It is odorless, tasteless, colorless, flexible, transparent, heat sealable, impermeable to oil, and good oxygen barrier properties [47]. Blends of pullulan with other biopolymers such as cellulose, chitosan, alginate, and starch have been reported having improved mechanical and thermal properties, low water absorption and low water vapor permeability [48]. Pullulan can be used as a coating for fruits and vegetables quality preservation more as a gas barrier instead of retarding water loss. Pullulan great advantage is in its capacity to lower O_2 and increase CO_2 in internal atmospheres of coated vegetables and fruits will reduce respiration rates, in so doing, extending the shelf life of fresh products in a similar way to modified and/or controlled atmosphere storage. Previous works have reported edible coatings produced from pullulan that was used to extend the shelf life of apples (Malinova and Champion cultivars) [49].

4.1.10 Xanthan

Xanthan gum is created by a sugar fermentation process, high molecular weight exopolysaccharide and is known as an important industrial biopolymer. Xanthan gum is the first microbial polysaccharide made by the culture fermentation of *xanthomonas campestris* on a polysaccharide backbone. This type of polymer consists of pentasaccharide repeating units containing D-Mannose, D-Glucose, acetyl-linked pyruvic acid, D-Glucuronic acid, and d-acetyl groups [50]. Xanthan gum is a very important exopolysaccharide made by *X. campestris* under controlled conditions [51]. The ability to control viscosity makes Xanthan be useful for food packaging. However, intensive researches still need to be carried out on its ability to fully stand alone as food-packaging material. Presently, blending with other biopolymer is recommended to produce good food package. High cost of production is another major challenge, facing its production.

4.2 Proteins

Proteins are macromolecules having specific amino acid, sequence, and molecular structure. According to Schmid et al. [52], films are typically made from proteins due to the facts that they are edible, supply nutrients, possess good mechanical barrier and visual properties. The protein-based films are strong oxygen barriers that

help to prevent food spoilage. When used in packaging, they could prevent food wastage during a lengthy chain of food distribution [53]. Proteins when combined with nano-clay fillers and other additives give stable products with greater strength and flexibility. Edible films extracted from protein are most attractive because of their higher barrier properties those obtained from polysaccharides and lipids. Protein-based films can be utilized for individual packaging of a small portion of food. Protein-based edible films are often derived from solutions of the proteins as the solvent/carriers evaporate. Protein films formed materials are derived from several animals and plant sources like egg, milk, and oil seed.

4.2.1 Soy Protein

Proteins that are isolated from soybean are known as soy protein. It is produced from soybean meal that has been defatted and dehulled. Soy proteins usage is dated back to the 1930s. It was stopped when synthetic polymer technology was introduced, and it is the first biopolymer from agriculture used for the manufacture of molded materials. According to Vroman and Tighzert [54], the major attribute of soy protein that is useful in food industries is texturizing and emulsification. Soy protein's concentrations are in three different concentrates; (i) soy protein flour (SPF), soy protein concentrate (SPC), and soy protein isolate (SPI). They are made up of globulins and albumins. Globulins are accountable for the hydrophobic and hydrogen bonding. Albumins' disulfide bonds are responsible for the polypeptide subunits binding [55]. Poor water resistance, thermoplasticity, and brittleness are among the major reasons for the limited usage of soy protein [56]. Plasticizers are frequently used to produce thermoplastic products and in addition, to enhance the flexibility of materials. Nevertheless, adding hydrophilic plasticizers makes soy protein to be vulnerable to water. Chemical modifications are alternative method to develop products with improved mechanical properties and water resistance. Blend of soy protein with biopolymers or reinforcement with natural fibers can be another helpful technological approach to produce soy-protein-based packaging materials. Figure 4 shows the production route (cycle) of soy-protein-based films.

Among biopolymers, SPI is a common by-product of the edible oil industry, which gave a broad range of potential applications in packaging, drug delivery, and mulching fields because of its abundance, low cost, sustainability, biocompatibility, and film-forming capacity [57–59]. According to Tian et al. [60], soy protein can be utilized in the manufacture of packaging materials, plastics, adhesives and can be a better alternative to the petroleum-based polymers.

Soy proteins are available in three different concentrations, flour (SPF) with 56% protein and 34% carbohydrate, concentrate (SPC) having over 65% protein and 18% carbohydrates, and isolate (SPI) with more than 90% protein and 2% carbohydrates. Soy protein film is generally produced from soy protein isolates rather than soy protein concentrates due to the fact that the non-protein fraction in soy protein concentrate adversely affects the film formability [61].

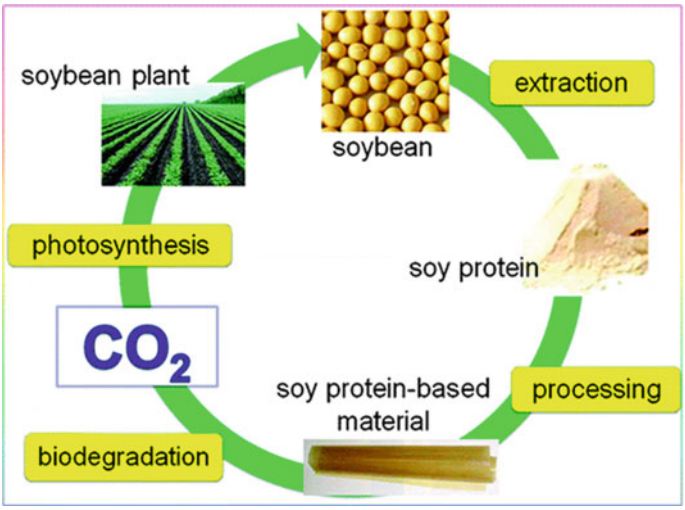

Fig. 4 Soy-protein-based film production cycle. *Source* Song et al. [88]

Soy protein plastics without any additive have inelastic characteristics, which causes processing difficult. Augmentation of plasticizers is an efficient way to achieve flexible SPI-based films. It is known that plasticizers with characteristics such as small size, high polarity, and more than one polar group per molecule generally impart great plasticizing effect on polymeric systems. Currently, biopolymeric films are usually plasticized by hydroxyl compounds [62]. Production of soy protein films is in two processes. Solution casting is the most commonly used, however, hot-pressing molding, which uncommon in the case of soy protein, is a more convenient one for industrial scale. Soy protein films are excellent gas barriers compared to that of lipids and polysaccharides. If they are not exposed to moisture, their oxygen permeability is at least 260 times lesser than that of low-density polyethylene, starch, and pectin.

4.2.2 Whey Protein

Whey protein is the ultimate protein source. It is the topmost protein quality available. Whey protein is a rich source of branched chain amino acids, having the most known levels that any natural food source can possess. Whey protein is one of two categories of protein that is sourced from milk (the other being casein protein). Whey is created as a by-product during the process of turning cow's milk into cheese. The whey-protein-based coatings and films are generally tasteless, flavorless, flexible materials, and water-based; the film varies from transparent to translucent subject to the formulation, composition, and purity of protein sources [63].

Whey protein is an important material that can be used to produce biodegradable and edible food packaging besides being applied directly to food (e.g., as fat replacer). For cheese production, a secondary product is whey and for years, it was regarded as an environmental pollutant and food waste due to little or no knowledge when it comes to the treatment of disposed waste in dairy industries. Composition of whey in increasing percentage contains mainly lipids (0.4–0.5% w/v), soluble proteins (0.6–0.8% w/v), lactose (4.5–5.0% w/v), and water (93%). Whey protein has good nutrition and the film-forming characteristic. In recent years, whey proteins have been attracting the attention of researchers. This is because they can be produced in transparent form. In addition, they are soft, and elastic. They are water-insoluble films, with good aromatic substances barrier property, grease barrier property, and oxygen barrier property in low humidity.

New biomaterial made of whey protein was developed as part of the EU-funded project. Whey layer is an alternative for petrochemical-based polymers, such as EVOH for manufacturing of barrier layers for food packaging [64]. This whey protein coating is biodegradable and improves the ability of multilayer films to be recycled [65]. It is already possible to produce products such as side-sealed bags, tubular bags, lid foils with a whey-protein-based barrier layer [66]. According to a survey of the Gesellschaft fur Verpackungsmarktforschung mbH (GVM, Germany) in 2010, there is not only increasing demand for film laminates but also for thermo-formable laminates. Apart from polyvinylidene chloride (PVdC), there is at present no replacement for EVOH for thermoforming applications.

Whey contains about 7% dry matter. The dry matter in order percentage includes <1% fat, ~3% organic acids, 8% minerals, 13% proteins, and 75% lactose. Whey-protein coatings were already tested just as edible films on it; among others like peanuts, fruits, salmon, or cereals, whereby whey coating presented good humidity, fat, aroma, and oxygen barriers. The process made it possible to improve and extend the shelf life of product, for instance, peanuts (by retarding the lipid oxidation causing rancidity). Furthermore, the edible films were observed not to alter the sensory properties of the coated products, while providing health benefits to the consumers.

4.2.3 Zein

In America, corn is the most and largest important agricultural commodity. Zein is one of the main components in corn, and it has long been researched upon for use as food and feed for livestock. Zein is a biodegradable and biocompatible material extracted from renewable natural resources; about 80% of the entire protein content in corn is zein. Zein is a complex and unique material, and it is among the few cereal proteins produced in a relatively pure form. For some reasons, the interest in zein is again gaining significant attention. Presently, the most successful and significant application of zein-based biodegradable materials in the food and pharmaceutical industries are as formulations and fibers acting as coating agents. The most promising application of zein appears to be for biodegradable coatings and films for packaging applications [67]. Zein as a matrix can be blended with a nano-bioactive

material possessing antioxidant or flavoring properties to fabricate an active package. According to Shukla and Cheryan [68], corn zein protein has been utilized because it is a good biodegradable and renewable material for package film forming, coatings, and plastic applications. Various researchers have proven that zein has better strength and lower gas permeability which are required for packaging applications than other biopolymer films. Zein films have shown great potentials as an alternative for commercial coating agents, like shellac and carnauba wax inside the food packets due to improved properties, like mechanical properties, biodegradability, water absorption, and gas barrier properties [69].

4.2.4 Collagen

In the food industry, collagen is mainly used because of its unique properties like film formation ability, biocompatibility, and resistance to organic solvent, short-time biodegradability, and non-toxicity. Collagen is the primary protein component of animal connective tissues. It is composed of various polypeptides, which contain mainly glycine, hydroxyproline, lysine, and proline. In both past and present, many researchers have developed films or coatings based on collagen to preserve food in a laboratory scale [70, 71]. Collagen fiber films have antioxidant properties and largely used in packaging of fish and meat [72]. Edible films in food products have great prospects in prolonging shelf life (taste, freshness, and quality) of foods fat, which may cause moldy and musty aromas. Collagen films are used as a barrier membrane to guard against the migration of moistures, oxygen, and solutes and ensure structural integrity and vapor permeability to the products. Gennadios et al. [73] studied wrapped beef cubes in collagen and frozen for 20 weeks and comparing them with wrapped control samples in terms of microbial, color, oxidation, and sensory attributes. The authors concluded that collagen is a possible alternative to plastic meat wrappings. However, the drawback with food packaging made from collagen is that they possess poor mechanical strength. In order to resolve the problem, Wang et al. prepared a novel and improved the food-packaging film, by reinforcing collagen matrix with sodium alginate, which acted as the reinforcing agent. The crosslinking agent used was glutaraldehyde to enhance the collagen film strength [74].

4.2.5 Gelatin

Gelatin is produced by hydrolysis of collagen [75]. Gelatin is a natural water-soluble protein distinguishable from its relatively not very strong odor and the random chain formation of the polypeptide in aqueous solution. Gelatin is obtained from the partial hydrolysis of collagen; a fibrous protein found mainly in specific parts of the invertebrate and vertebrate animals, such as skins, bones, tendons, and connective tissues [76]

(1) Type A: with an isoelectronic point at a pH of between 8 and 9 and obtained from acid treated collagen and (2) type B: with an isoelectronic point at a pH of

between 4 and 5, derived from an alkali-treated precursor which converts asparagine and glutamine residues into their respective acids, resulting in higher viscosity [61]. Edible film from gelatin is produced by dissolving gelatin in hot water, after a total dissolution is observed, the solution is spread on for casting before finally dried in oven [9]. Tray gelatin is first dissolved in hot water. The dispersed solution is poured on a plate or a tray for casting. Finally, the solution is dried in an oven to get an edible film [9]. Gelatin-based edible films are thick, have high protein content, and higher increase in mechanical properties, however, they decline in water vapor permeability capacity. They increased mechanical properties, but their water vapor permeability decreases [77].

5 Aliphatic Polyesters

Aliphatic polyesters are a very important class of biodegradable polymers; many of aliphatic polyesters have excellent biocompatibility and biodegradability properties. There are many types of aliphatic biodegradable polyesters but very little are in commercially available. Those that are currently focused on by researchers for commercial use are: polyglycolic acid (PGA), polylactic acid (PLA), poly-ε-caprolactone (PCL), poly(3-hydroxy valerate), and polyhydroxybutyrate (PHB). Among these polymers, PLA and PHB are possibly the most widely studied biodegradable thermoplastic polyesters. Both are biocompatible, biodegradable, and there melting point are relatively high between 160 and 180 °C. Nevertheless, their brittleness and narrow processing window limit their practical applications. Therefore, many studies have recommended blending them with other natural polymers.

5.1 Polyhydroxybutyrate (PHB)

Polyhydroxybutyrate (PHB) is a polymer originating from bacteria that can be broken down by an enzyme such as PHB depolymerases [78]. Polyhydroxybutyrate (PHB) has several advantages over conventional petrochemically derived plastics. PHB is sourced from renewable natural resources. PHB has shown great potential for applications in food- and medical-packaging materials [79].

PHB has improved physical properties than polypropylene, which is good for food-packaging applications and is, absolutely, non-toxic. PHB's low impact strength is resolvable by incorporating hydroxyvalerate monomers into the polymer producing polyhydroxybutyrate-*co*-valerate (PHBV) that is commercially marketable with trade name "Biopol." Just like PHBV and PHB, it completely degrades into carbon dioxide and water under aerobic conditions. Despite these merits, the drawback is processing PHB into flexible thin films; this is one of the main limitations that prevent its widespread application. The melting point is high (175–180 °C) and low degradation temperature of ~220 °C; limits the potential during thermal process-

ing for the preparation of PHB films [80]. Packaging produced from PHB has poor impact resistance, which led to the low usage of PHB for food-packaging applications. Another main factor limiting the usage of PHB is due to the high production costs when compared with other plastics made from petrochemicals. PHB presents the benefits of biodegradability, even though market expectations remain high for the production of PHB-based biomaterials that possess good potential as an alternative for PP in bags, bottles, plates, and film applications.

5.2 Polylactic Acid (PLA)

Poly(lactic acid) (PLA) is a biodegradable polymer that is obtained or sourced from agricultural products like sugarcane, corn, and other sources [81]. Results obtained from various experiments showed that PLA imitated in use for the application of gas barrier films to be used for the food- or medical-packaging materials because it has relatively low resistance to oxygen and water vapor permeation compared with conventional non-degradable polymer resins [82]. Also, high price and brittleness of PLA lower the possibility of its commercialization. Therefore, blending PLA with other suitable biodegradable polymers, which has comparably better flexural properties, excellent impact strength, will modify various properties and contribute toward low overall material cost [83]. Several developments in North America and Europe that involve the use of PLA as packaging materials for supermarket products have been reported. PLA-based containers have found useful applications for the packaging of foods such as Biota™ PLA-bottled water; Noble™ PLA-bottled juices, and Dannon™ yogurts. These containers meet the EU and German food grade requirements. The special features of PLA, such as biodegradability, GRAS status, and bioresource, put PLA in a distinctive position for applications in the food industries. An antimicrobial packaging system centered on PLA would be better than other antimicrobial systems due to factors such as cost-effectiveness, fewer regulatory concerns, effective antimicrobial activity, and environmentally friendliness. Although PLC potential for antimicrobial packaging has not yet been explored extensively, further study and development is necessary in order to full harness the potentials of such materials [84].

6 Future Trend

Environmental factors, costs, and disposal of waste generated by plastics are of major concern to the global community. Plastic is in virtually everything we buy. Part of the side effects of chemicals used in producing plastic package to human health is that they are linked to hormone disruption, genital malformations, reduced fertility and cancer-combing in a ghastly synergy to produce body-warming effects [85]. These hazards created by plastic do not only affect human but also live in the ocean. The

amount of plastic waste entering the oceans from the land yearly exceeds 4.8 million tons (Mt), and these quantities have the potential of increasing inputs of plastic waste into the oceans as high as 250 million tons (Mt) by the year 2025 [86].

It is time for everyone to stand up to this global challenge before global warming finally wipes off the earth. In December 2016, China which is the destination of almost all the plastic waste in the UK announced a ban on any form of plastic waste from anywhere across the world. This implies that every country now needs to focus on its packaging material's production on raw materials that are easily degradable.

Presently, researches on food-packaging materials now focus on using renewable materials that are much more environment-friendly due to the need to find a replacement for fossil-fuel-based polymers. Every day, more and more technologies are put in place for food-packaging materials to be totally saved for consumers. The overall focuses are on the production methods, material properties, and commercial applications.

However, despite these merits, there are still some shortcomings, which prevent the wider commercialization of biopolymers in food-packaging applications. These drawbacks are mainly due to material performance and price in comparison with their traditional counterparts, which remains a major challenge for bio-based polymers. However, it may take another 20 years to fully actualize the potentials in biopolymers as food-packaging materials. From now, not all stakeholders in agricultural and food industry should see the use of biopolymers in food packaging as an option but a necessity.

7 Conclusion

The growing waste volume globally is a major concern for humanity. Before now, many of the packaging materials used in the food industry are non-biodegradable. Disposal of these materials after use is a major concern, and most of them take hundreds of years before finally decomposing. For example, plastic bottles may take up to 450 years to completely degrade. The best option to deal with the problem is avoiding products that contribute to waste materials that decompose more than a year in the landfills through down to business design from natural materials. The primary driving factors for the development of biodegradable food-packaging materials include crude oil prices, consumer demand a better and more friendly and convenient packaging among others. Recently, biopolymers have become an important class of materials for food-packaging applications. Since they are natural polymers, there is no concern about the materials directly getting in contact with food because they do not post any threat to health. As discussed in this chapter, the commonly used biopolymers for food packaging are: polysaccharides, proteins, and aliphatic polyesters.

Even though most of these biopolymers have weak mechanical and physical structures, many studies carried out suggested blending of different biopolymer types in order to enhance great improvements in their structures. The current observable trend

for food packaging is the method of blending various biopolymers such as starch-PCL blends, starch-PLA blends, just to mention a few. Bottles, buckets, jars, drums, vials, pails, cans, barrels, closures, caps, aerosol parts, food containers, packaging films, disposable cups, coating for varieties of packaging, packaging bags, institutional and household refuse bags and film, and baskets and boxes are being produced from biodegradable polymers.

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Chapter 7
Nanostructured Green Biopolymer Composites for Orthopedic Application

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1 Introduction

Accidents and diseases are irrefutable in the course of human existence. However, their occurrence and ensuing consequences can be significantly minimized, through modern medicine and appropriate lifesaving technologies. The majority of these accidents, most of which usually lead to death, are caused by road accidents, plane crash, ship capsize, building collapse, and fire [1]. Wars and natural disasters—earthquakes, tsunamis, sandstorms, floods, famine, and diseases—are also on the upper level of this hierarchy of death [42, 77]. According to an online article published by World Health Organization (WHO) in 2015 on global road safety status [151], data from 180 nations show that worldwide, the annual death toll from road accidents has leveled at 1.25 million, with the foremost occurrence happening in developing countries.

As far as diseases are concerned, cancer is one of the world's most prominent causes of morbidity and death, with around 14 million new cases in 2012. In about

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twenty years' time, experts have revealed that this number is anticipated to rise by approximately 70%. Cancer takes second place amid the causes of death globally and accounted for 8.8 million deaths in 2015, and approximately 1 in 6 deaths is linked to cancer worldwide [138].

To continue living, the surviving victims of these accidents and diseases (most especially in cancerous cases) might need to undergo amputation or reconstructive surgeries [148]. The total number of persons with an amputation and those using prosthesis are envisaged to increase by at least 47% by the year 2020 [70]. Recently, released data from the American Society of Plastic Surgeons (ASPS) have summarized cosmetic and reconstructive procedures performed in 2016 [111]. According to these statistics, the total number of reconstructive procedures by ASPS member surgeons has remained relatively stable at 5.8 million annually since 2015. Furthermore, the ever-increasing obsession of twenty-first-century celebrities and gender-troubled individuals for plastic surgeries (maxillofacial, hips, and genital modification surgeries) cannot be ignored. As indicated by the yearly plastic surgery procedural measurements, there were 15.9 million careful and insignificantly obtrusive restorative surgeries performed in the USA in 2015, a 2% expansion more than 2014. All these challenges require a new dimension to orthodox medicine and surgery for success.

On the bright side, the consolidation of modern medicine, surgical technologies, biomedical engineering and materials science and engineering has proven worthy to be the key to the besought success [36, 47, 88]. In this regard, laboratory-developed biomaterials have a major role to play; thus, a thorough investigation into their syntheses and feasible applications is crucial [75, 114]. The early applications of natural materials as biomaterials in medicine dated back to the primeval times of the Egyptian physicians who were using plants and animal product-based materials as sutures for accelerated wound healing [95]. Consequently, the resurgence of the steam engine that accelerated the industrial revolution of the eighteenth century came along with a downside of increased rate in the types and nature of accidents. Usually, minor accidents were attended to, in the conventional ways, however critical accidents such as crushed bones called for a more advanced approach [20]. This gave birth to the replacement of bones by wax, decalcified bones, glass, acrylic, rubber, and later iron as these were the major materials prevalent then. Unfortunately, the issues of biocompatibility arose and thus orthopedic surgeons became ruminative about possible solutions [50]. Shortly after, the ideology to use metallurgical processing routes to modify the properties of iron for biomedical advantages became known. Afterward, a switch was made to stainless steel; however, this approach was not totally long standing since the issues of stainless steel corrosion and its adverse chemistry in the host's body soon became a chronic challenge [45]. This has been discredited, due to the reaction between the stainless steel and the constituents of the biological fluids contained in the human body [45, 50]. Some authors have also claimed that the temperature of the human physiological fluids has the tendency to facilitate the corrosion of stainless steel in the human body [23].

Nonetheless, researchers were not dispirited; they persisted in burning the wicks of their scholastic candles at both ends to transcend the afore-stated limitation of stainless steel. Impressively, their research findings soon landed on a treasure trove

and the nickel titanium (Nitinol) shape memory alloy (SMA) was serendipitously discovered. It later became the gold standard biometallic material for implants [64]. The exceptional properties of this material include, but not limited to excellent biocompatibility, attractive mechanical properties and excellent corrosion resistance. To date, this material is still widely employed as biomedical implants [123].

As customary with research, another school of thought has arguably claimed that the huge expenses concomitant with the production of Nitinol counteract its economic feasibility as an outstanding biometallic material; hence, a critical and succinct review is required. They claimed that this drawback has rendered it a material for the bourgeoisie and not the proletariat [4]. Accordingly, in the quest to address the issue concerning the economic viability and availability of Nitinol, intensive research into synthetic polymers and their composites as suitable alternatives was spawned [39]. Several authors have published and patented a remarkable volume of useful research findings on synthetic polymers, their composites, and their biomedical applications [39]. Their properties such as low density, appreciable mechanical strength improvable by physical and chemical modifications [39], chemical inertness, corrosion resistance, inexpensiveness, and ease of processability make them very useful as promising biomaterials [39]. One of the synthetic polymers that have gained wide acceptance as a structural implant material is ultra-high-molecular-weight polyethylene (UHMWPE) that offers a large array of attractive properties that are required of a structural biomaterial [97]. However, it is susceptible to time-dependent tribomechanical property degradation with consequences of aseptic loosening and osteolysis [130]. However, on a positive note, gamma irradiation and filling UHMWPE with the bioceramic hydroxyapatite (HAP) can be used to surmount these limitations to a reasonable extent [17, 92]. Other synthetic polymers that are in use for biomedical polymers are high-density polyethylene, polyurethane, and polytetrafluoroethylene [39]. They can be blended with each other or combined with bioceramics and biopolymers, for the improved properties and functionalities required for biomaterials [39, 92].

Although synthetic polymers have evinced numerous advantages and prospects as promising precursors for biomaterials synthesis, their sustainability and environmental impacts cannot be overlooked [14]. The major feedstock for synthetic polymer production is obtained from fossil origin. Reports from the crude oil experts are emerging each year, revealing that if the current exponential demand for synthetic polymers at the present rate persists, this demand would outpace the feedstock reserve [14]. Thus, it is now essential to turn to renewable sources for polymer production. Correspondingly, the negative environmental impacts constituted by synthetic polymers by the vices of their disposal problems (they are not biodegradable), carbon footprint promotion (hydrocarbon origin), and greenhouse effect creation would also rationalize the switch from these polymers to renewable and eco-friendly alternatives [14]. Fortunately, nature has made these alternatives abundantly available as natural biopolymers primarily derivable from plants, animals, and specific species of microorganisms [169].

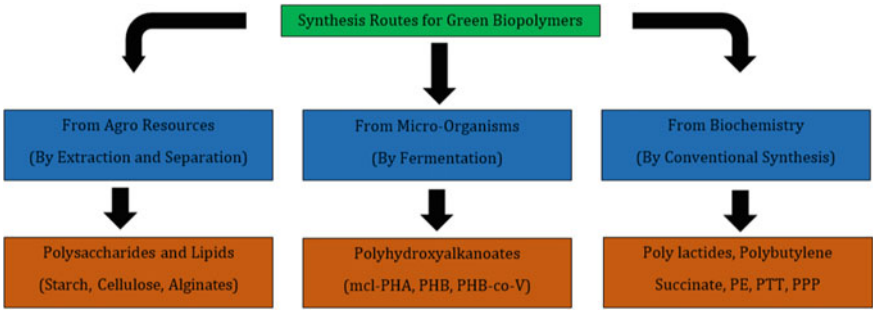

Fig. 1 Typical examples of green biopolymers synthesized via various processes

2 Green Biopolymers

Until now, there is still a cloud of ambiguity around the definition of "biopolymers." Some authors have defined them as polymers that have their origin as biological sources [101]. Others have claimed they are polymers synthesized from living organisms. They have also been described to be polymers that are designed to be biodegradable via the actions of living organisms [15]. For the sake of simplicity in this study, they are described as polymers from bioresources that are synthesized and can be exterminated through eco-friendly routes; i.e., they pass through a green pathway from cradle to grave. In this context, they are broadly classified into three types, namely polysaccharides, proteins, and green polyesters. Intensive research findings in the foregoing regard have shown that these classes of materials possess a wide spectrum of advantages over their synthetic counterparts, which in turn renders them suitable materials for a plethora of biomedical applications. Some of these advantages include, but not limited to, biodegradability, biocompatibility, low toxicity to non-toxicity, carbon neutrality, economic viability, easy processability, sustainability, and environmental friendliness [44]. Common biopolymers and their syntheses pathways are presented in Fig. 1.

2.1 Polysaccharide-based Biopolymers

Polysaccharides are essentially carbohydrates gotten from inexhaustible resources, essentially plants, animals, and microbes which are naturally available in ample quantity. The building block of polysaccharides is monomers of saccharides linked together by *O*-glycosidic chains. Their physical properties such as viscosity, solubility, and interfacial properties are essential, dictated by their difference in monosaccharide composition, molecular weight, chain morphologies, and linkage types and patterns. Different types of polysaccharide-based biopolymers include starch, cellulose, chitin–chitosan, alginate, dextran, and hyaluronic [11, 15]. They are natural

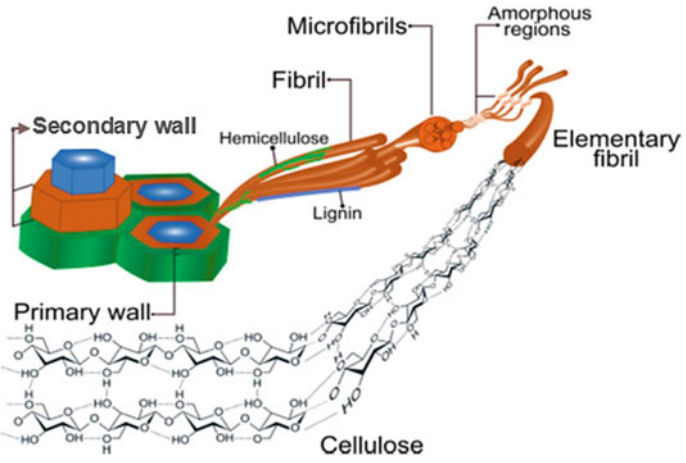

Fig. 2 Stratified structure of plant cellulose [119]

products that the body system is familiar with; therefore, they have a very significant role to play as biomaterials without compromising the hosts in any negative ways whatsoever.

Cellulose

Cellulose, a carbohydrate biopolymer frequently connected with hemicellulose and lingo-cellulose, is the richest bio-macromolecule in the biosphere. It was first segregated and tested in 1838, and in this way, restrictive investigations and overviews have been completed on its properties [9, 99, 119]. Cellulose consists of β-D-anhydroglucopyranose monomers covalently linked together by acetal works between the central gatherings of the C4 carbon atom and the C1 carbon atom (β-1, 4-glycosidic bonds). The aforementioned linkage is responsible for the resistance to chemical and enzymatic attacks [9]. Cellulosic biopolymers for industrial and pharmaceutical applications are usually synthesized by various chemical modifications of cellulose. The major cellulosic biopolymers for industrial and pharmaceutical applications are cellulose esters, cellulose ethers, and regenerated cellulose. Due to its biodegradability, biocompatibility, remarkable mechanical properties, and low cytotoxicity, there is an incredible enthusiasm to develop biomedical materials based on cellulosic starting point [9, 99, 119, 157]. The various leveled structures of cellulose separated from the plant are presented in Fig. 2.

However, for biomedical purposes, highly pure cellulosic biopolymer (biopolymer that contains no other constituents) is synthesized by using groups of algae, a number of microbial varieties (*Escherichia*, *Acanthamoeba*, and so on.), and tunicates in the animal kingdom. Microbial cellulose is a polysaccharide excreted extracellularly by the above-mentioned bacteria. The species *Gluconacetobacter xylinus* (or *Acetobacter xylinum*) is the most broadly contemplated cellulose-producing bacteria [157]. The microfibrillar and nanostructured arrangement of bacterial cellulose

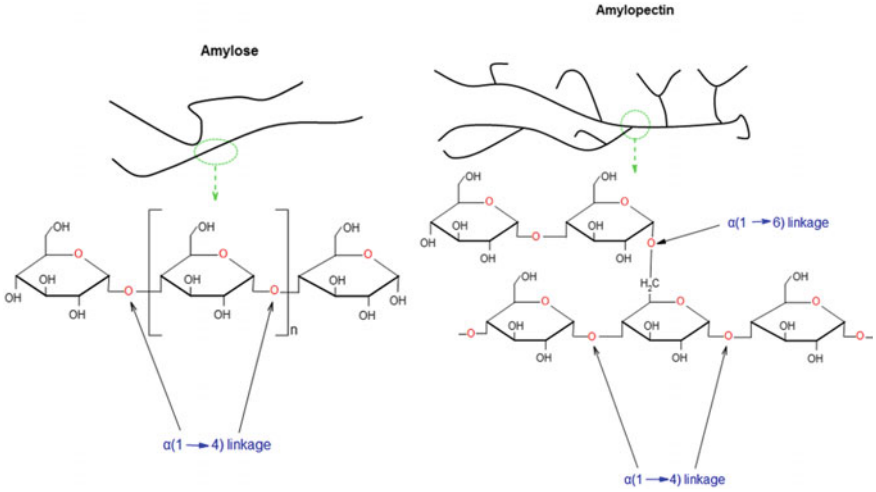

Fig. 3 Molecular structures of starch: (left) amylose and (right) amylopectin

gave it better biocompatible and mechanical properties than that of plant-derived cellulose. The biomedical applications of bacterial cellulosic biopolymers and their blends/composites are seen in wound dressing, accelerated wound healing, scaffolds for tissue/cellular engineering and regenerative medicine [119, 157].

Starches

Starches are a unique class of biopolymers occurring in nature. Plants enzymatically produce them, as an energy means in the form of discrete granules (they are gotten from carbon dioxide and water, by photosynthesis in plants). It is the primary energy store in higher plants, and for a long period of time it is stored in certain parts of the plants (seeds, stems, roots, etc.) which in turn allows the formation of enormous granular structures. Commercially, the foremost sources of starch are grains and tuber crops. Structurally, starch is made of linear amylose polysaccharide and highly branched amylopectin polysaccharide. Amylose accounts for about 10–30% of the granule, and amylopectin accounts for the remaining 70–90% [72]. Amylose is a linear polymer formed by long chains of α(1–4)-linked d-glucose units with a polymerization degree range of 300–10,000 dependent on its botanical origin [89]. Amylopectin is a polymer with very high molecular weight. It has the same backbone structure of amylose but has many α(1–6)-linked branch points [32]. The various structures of amylose and amylopectin are presented in Fig. 3.

Amid the polysaccharide-based biopolymers, starch is one of the auspicious materials for use in bio-absorbable composites, attributable to its copious supply, inexpensiveness, great processability, hydrophilicity, biodegradability, and simplicity of physical and chemical modifications. When blended with different materials, it changes the execution and properties of a definitive mix because of its hydrophilicity. Furthermore, starch and its subsidiaries have better reactivity in comparison

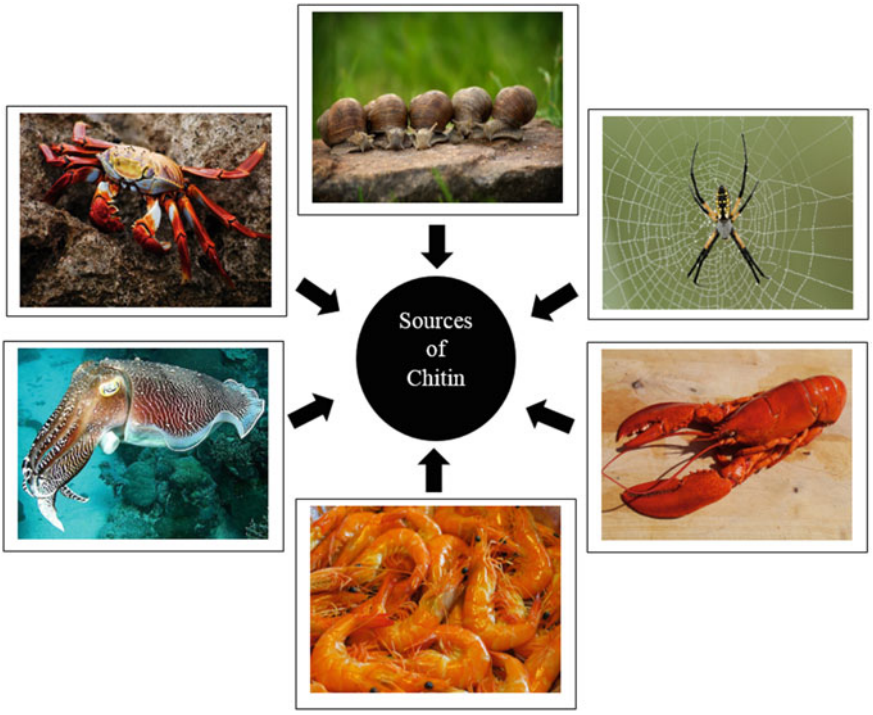

Fig. 4 Sources of chitin

with polysaccharide-based biopolymers, for example, cellulose and chitin. Starches and their blends/composites are used in the following biomedical applications: bone cement, bone filler in orthopedics, bone replacement/fixation implants, and drug delivery [32, 72, 89].

Chitin and Chitosan

Chitin

Chitin was the first polysaccharide-based biopolymer known to man before cellulose was discovered in 1838. In terms of polysaccharide abundance in nature, it comes after cellulose and a huge amount of this bio-macromolecule can be found in exoskeletons of crustaceans/arthropods—crabs, lobsters, shrimps, radula of mollusks and cuticles of insects, internal backbone and beaks of cephalopods, spiders' webs, and fungi cell walls [8, 74, 93, 94, 128, 155]. Figure 4 presents the commercial sources of chitin.

Chitin is a highly basic high-molecular-weight linear polysaccharide (it has a mean molecular weight (MW) that ranges between 1.03 × 106 and 2.5 × 106 Da) consisting of copolymer repeated units of β-(1→4)-2-acetamido-2-deoxy-β-D-glucose and β-(1→4)-2-amino-2-deoxy-β-D-glucose [8]. The structure β-(1→4)-N-acetyl gly-

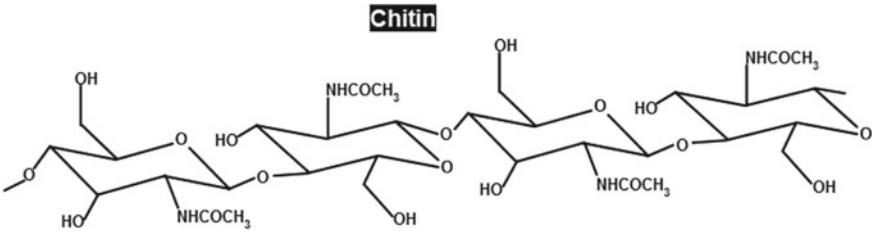

Fig. 5 Structure of chitin [8]

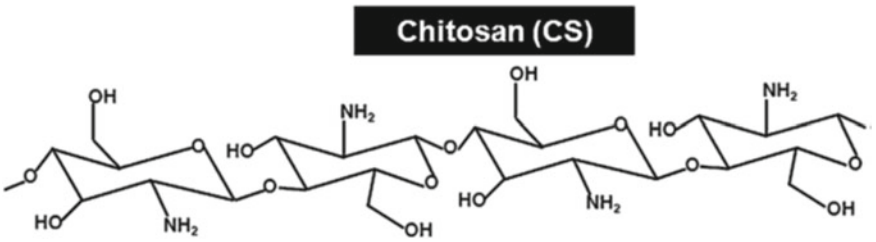

Fig. 6 Structure of chitosan [8]

cosaminoglycan found in chitin with two hydroxyl groups and an acetamide group is responsible for the high crystallinity in chitin with strong hydrogen links. It has a highly organized crystalline microfibril structure and is made up of an aggregation of nanofibers with a diameter of 2–5 nm and a length of about 300 nm [8, 74, 128]. This polysaccharide has three crystalline forms, based on the origin of chitin. The predominant form of α-chitin is present in the exoskeleton of shellfish and cell walls of fungi. In this crystalline form, the chains of chitin are arranged in an antiparallel structure, which gives room for the formation of orthorhombic crystal that confers firmness to the polymer. In the form of β-chitin, the chains, like cellulose chains, are aligned in parallel and form monoclinic crystals. In this circumstance, intramolecular hydrogen bonds prevail over intermolecular interactions. β-Chitin is usually linked to squid protein and diatomaceae characterized by frail packing. Finally, there is a form of γ-chitin, which is a combination of the α and β forms. γ-Chitin exhibits the attributes of both polymorphisms and swells when in contact with water [8, 74, 94, 128, 155].

Although it is widely available, the use of chitin is limited due to its bulk structure and its inability to dissolve in water and most organic solvents [74]. Chitin is usually used as a precursor for the synthesis of chitosan through deacetylation. This is due to its insolubility in the above-mentioned media. Figures 5 and 6 show the structures of chitin and chitosan, respectively.

Chitosan

Chitosan, consisting of randomly distributed poly-β (1→4)-2-amino-2-deoxy-D-glucose monomers, is a linear semicrystalline amino polysaccharide and a cationic

biopolymer derived from the full or partial *N*-deacetylation of chitin. One common route of obtaining chitosan is by treating chitin with sodium hydroxide, which is also a biocompatible, biodegradable, non-toxic, antimicrobial, and hydrating agent [74, 128, 155]. Chitosan possesses a large array of attractive properties, which has made it an eye-catching biopolymer for various applications in food processing industries, pharmaceutical companies, and biomedical engineering. Some of these attractive properties include but not restricted to low toxicity, biocompatibility, antimicrobial activities, biodegradability, bioactivity, pH sensitivity, high charge density, hydrophilicity, mucoadhesion, good film-forming ability, and excellent processability. Biomedical applications of chitin include scaffolds for tissue engineering, biomaterial-hydrogels and biosensors for biomedical devices and pharmaceutical ingredients. The cheapest source of chitosan is squid pen, which is obtained as waste in the squid processing industry [8, 74, 128, 155].

Alginic Acid and Alginate

Alginic acid is a precursor of the alginate biopolymer. It is an anionic, strictly unbranched copolymer of mannuronic acid (M block) and guluronic acid (G block) units arranged in an asymmetrical pattern of varying proportions of GG, MG, and MM blocks as shown in Fig. 7. Alginates can be synthesized from alginic acid via enzymatic catalysis. Alginates are straight platform biopolymers comprising of 1,4-connected -D-mannuronic corrosive (M) and 1,4 -L-guluronic corrosive (G) filtrates organized in homogenous (poly-G, poly-M) or heterogenous (MG) block-like. They are polysaccharides gotten from the cell wall of brown algae (see weeds), including Macrocystis pyrifera, Laminaria hyperborea, Ascophyllum nodosum [93, 135], and numerous soil microbes, for example, Azotobacter and Pseudomonas. Alginates are not arbitrary copolymers, but rather as per the source green growth comprise of blocks of comparable and entirely alternating filtrates (that is, MMMMMM, GGGGGG, and GMGMGMGM) (Fig. 7), every one of which has distinctive conformational inclinations and conduct [133]. Sodium alginate is the most ordinarily utilized alginate shapes in the industries since it is the first by-product of algal purification. Sodium alginate comprises of α-l-guluronic corrosive deposits (G blocks) and β-D-mannuronic corrosive filtrates (M blocks), and in addition portions of substituting guluronic and mannuronic acids. Alginate-containing products are used for wound dressings, especially to make hydrophilic gels over injuries, which can create agreeable, restricted hydrophilic conditions in healing wounds. Furthermore, dental impressions made with alginates are easy to deal with for both dental specialist and patient as they quickly set at room temperature and are financially savvy [93, 135, 133].

2.2 Protein-based Biopolymers

Proteins

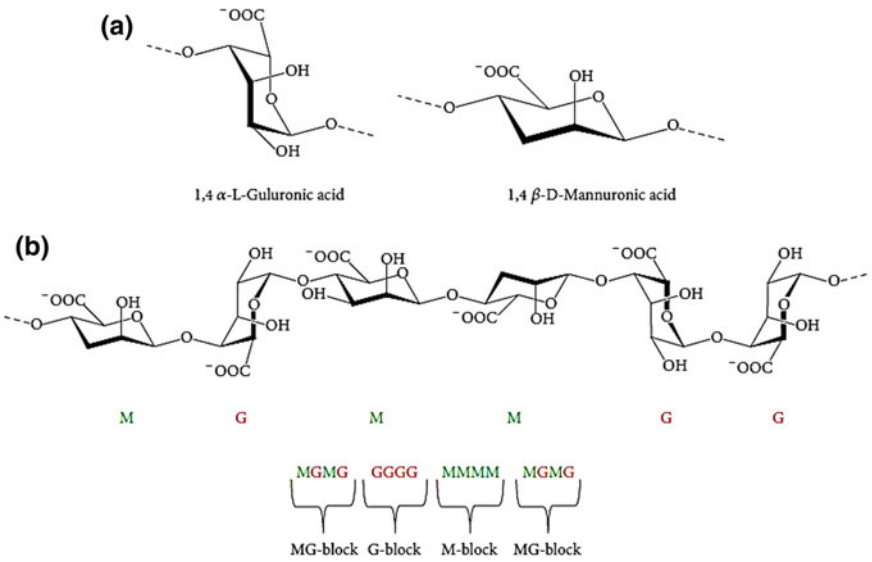

Fig. 7 Structure of ALG: monomers (**a**), chain conformation (**b**), and block distribution [135]

These are vast natural polymeric macromolecules, comprising of at least one long chain of amino acid filtrates. Proteins play out various capacities inside living beings, including catalyzing metabolic responses, DNA replication, reacting to stimuli, and transporting atoms starting from one area, then onto the next. Proteins vary from each other basically in their arrangement of amino acids, which is administered by the nucleotide succession of their genes and which ordinarily shows protein collapsing into a particular three-dimensional structure that decides its action [53, 66, 142]. A straight chain of amino acid deposits is known as a polypeptide. Smaller chains are called oligopeptides. Like other natural macromolecules, for example, polysaccharides and nucleic acids, proteins are basic parts of life forms and take part in basically every procedure inside cells. Numerous proteins are catalysts that catalyze biochemical responses and are crucial to digestion. Proteins additionally have basic or mechanical capacities, for example, actin and myosin in muscle and the proteins in the cytoskeleton, which frame an arrangement of the platform that keeps up cell shape [53]. Proteins are also vital in cell flagging, insusceptible reactions, cell grip, and the cell cycle. These attractive biomedical properties of protein tremendously stimulated the interest of researchers for multifaceted applications [44]. The common protein-based biopolymers used for green biopolymer synthesis are discussed below.

Keratin

Keratin represents the most inexhaustible structural proteins in epithelial cells and, together with collagen, is the most imperative biopolymer in creatures. It is among the hardest organic materials, having both high strength and high modulus, in spite of

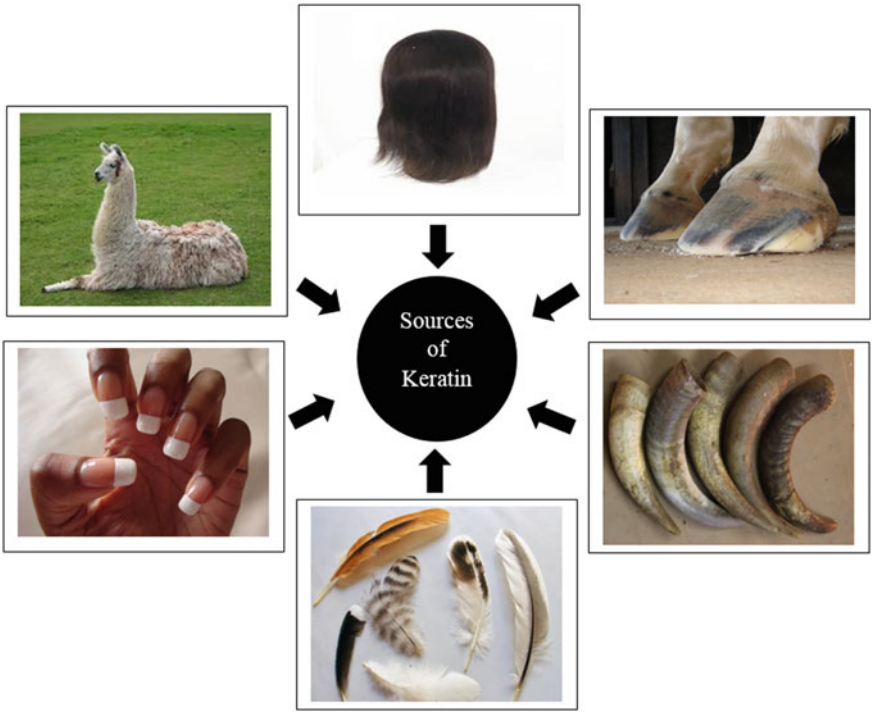

Fig. 8 Sources of keratin

the fact that it is exclusively made out of polymeric constituents, and rarely contains minerals [132]. Keratinous materials, formed by particularly sorted out keratinized cells loaded up with stringy proteins (keratins), are natural polymeric composites that display a complex various leveled structures running from nanoscale to centimeter scale: polypeptide chain structure, fiber lattice structure, lamellar structure, sandwich structure. They make the hard integuments out of creatures, e.g., epidermis, fleece, plumes, horns of warm-blooded creatures, and additionally quills, hooks, and snouts of feathered creatures and reptiles, and viably serve an assortment of capacities, for example, for security and guard, predation, and as protective layer [43, 132, 143] (Fig. 8).

Keratin refers to a category of structural proteins that are durable, insoluble, and self-assemble to intracellular bundles of intermediate filaments. It is the main connective tissue inside the epidermis and has an imperative impact in the last phase of wound healing. Keratin consists of polypeptide chains formed via the condensation of distinct amino acids. It is a basic protein portrayed by high cystine content and a lot of hydroxyl amino acids, particularly serine. It is described by the presence of a series of non-covalent bond (electrostatic powers, hydrogen bonds, hydrophobic powers) and covalent bond (disulfide securities), which are hard to be impaired. It is a structural protein characterized by high cystine content and a significant amount of

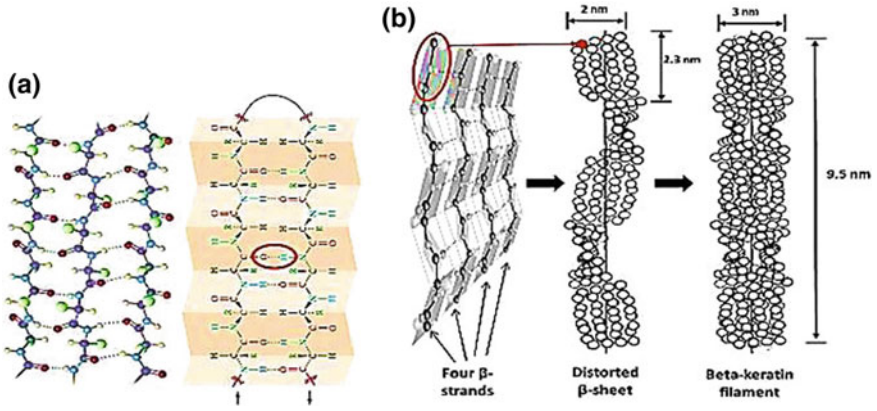

Fig. 9 Intermediate fiber structure of α-keratin: **a** ball-and-stick model of the polypeptide chain and α-helix, **b** schematic illustration of the transitional fiber arrangement [143]

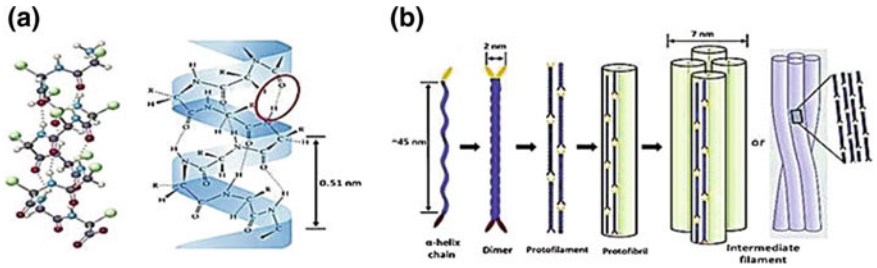

Fig. 10 Structure of the beta-keratin fibers: **a** ball-and-stick model of the polypeptide chain and description of the pleated beta sheet, and **b** schematic illustration of the development of beta-keratin fiber [143]

hydroxyl amino acids, especially serine. Keratin has a high concentration of cysteine, 7 to 20% of the total amino acid residues that form inter- and intramolecular disulfide bonds. α-Keratin (Fig. 9) with helical structures declines, and β-keratin (Fig. 10) appears upon stretching elastin, which affects mechanical, thermal, and chemical properties [43, 132, 143].

Delicate keratins are parts of the vast majority of the eukaryotic cell grids, while hard keratins are found in defensive tissues, for example, nails, hair, fleece, quills, horns, and feet of numerous sorts of creatures. In light of their biocompatibility, biodegradability, and non-poisonous quality, keratins and their subsidiaries are broadly, utilized for biomedical applications [125, 143]. Keratin laminates and keratin-based laminates are utilized in visual surface reconstruction, drug delivery system, and treatment of intense myocardial dead tissue. Keratin hydrogels are utilized in fringe nerve fix and as homeostatic operators. Keratin powders are utilized in wound recuperating and bone recovery. Furthermore, the utilization of keratin in tissue-building frameworks has been appeared to upgrade cell connection and expan-

sion, and to enhance the biomaterial's cell and tissue biocompatibility, both in vitro and in vivo [103].

Collagen

Collagen is the most inexhaustible protein in creatures and the fundamental basic segment of the extracellular network, with (Gly-X-Y)n repeating units longer than 1400 amino corrosive deposits and with three build-ups for every one helical turn structure. The most widely recognized tripeptide unit of collagen is (Gly-Pro-Hyp). Collagen is the major insoluble fibrous protein in the extracellular grid and in connective tissue; because of its intricate structure, it gives the key basic and mechanical support to a few tissues. It is a noteworthy auxiliary protein, forming molecular lines that reinforce the ligaments and vast flexible sheets that help the skin and interior organs [11, 139]. Teeth, and additionally bones, are made of collagen and mineral gems, for the most part hydroxyapatites. Collagen gives structure to every creature's body, securing and supporting the gentler tissues and interfacing them with the skeleton. It is the absolute and most abundant protein in the set of all animals. There exists about 27 types of collagen, and the structures all serve the same purpose: to enable tissues to withstand stretching. The most richest sources of collagen are cow skin, and pork and cows' bones. Collagen is a standout among the most helpful biomaterials because of its biocompatibility, biodegradability, and powerless antigenicity [3]. The primary use of collagen films in ophthalmology is as medication conveyance system for moderate release of fusing drugs. It was additionally utilized for tissue building, including skin substitution, bone substitutes, and artificial blood vessels and valves [3, 139].

Gelatin

Gelatin is a polyampholyte/denatured biopolymer gotten from collagen by the procedure of corrosive or soluble hydrolysis or by means of chemical–thermal degradation process with a lot of amino and carboxyl gatherings on its subatomic chains. Gelatin shows innate cationic nature at pH values beneath its isoelectric point through protonation of amino groups [124]. The isoelectric purpose of gelatin can be altered amid the manufacturing process to yield either a contrarily charged acidic gelatin or a positively charged fundamental gelatin at physiological pH. Gelatin is a heterogeneous combination of single- or multistranded polypeptides containing an amino corrosive build-up run from a hundred to a couple of thousand (300–4000). It has both positive and negative charged residues and also hydrophobic groups (rough proportion 1:1:1) that drive this polypeptide particularly for biomedical applications [110, 124]. This property hypothetically permits electrostatic associations between a charged biomolecule and gelatin of the contrary charge, forming polyion complexes. In tissue building, drug delivery, and bio-imaging research, gelatin has received a lot of attention because of its biological origin, excellent biodegradability, biocompatibility, plasticity, protein affinity, adhesive strength, and commercial availability at low cost. Furthermore, gelatin is non-immunogenic and non-carcinogenic, and it displays low antigenicity. Different types of gelatin carrier networks have been

accounted for use in the controlled discharge applications, while portrayal contemplates have demonstrated that gelatin carriers can sorb charged biomolecules, for example, proteins and plasmid DNA [108, 110, 124].

Silk and Silk Fibroin

Silk

Silk is a normally occurring fibrous protein created by an assortment of bug-silk worm covers, scorpions and arachnid-cobweb. Silk is degradable and lightweight with magnificent warm and mechanical properties. Silk is characterized by a very dull essential arrangement that prompts noteworthy homogeneity in secondary structure, i.e., triple-helix ß-sheets (Fig. 11) [76]. A few highlights of silk-based materials, for example, mechanical properties, solvency, and biodegradability, can be controlled by controlling the optional structure. Silk can, without much of a stretch, be separated and decayed ordinarily. Silk comprises of two parts, fibroin (80 %) and sericin (20 %) [80]. Fibroin is a water-insoluble protein with a profoundly arranged crystalline structure, and sericin is a sticky substance which is evacuated amid degumming process; it is one of the causes for prompting a fiery response. Silk is extensively named wild silk (Eri, Tasar, Muga) and local silk (mulberry). In the mulberry silk (Bombyx mori), glycine, alanine, and serine establish around 82 % of the amino acids, while it is 73 % in the non-mulberry silks with a high extent of alanine. The hydrophilic to the hydrophobic amino corrosive proportion for non-mulberry silks (9.06–9.85) is higher when contrasted with that of the mulberry assortments (5.29–6.22), which results in higher dampness substance of non-mulberry silks. Common silk fiber offers high strength-to-weight proportion [76, 80, 96]. Certain silk strands have mechanical properties better than nylon, Kevlar, and high-tractable steel. Another age of materials dependent on this normal polymer may have numerous potential applications. Impenetrable vests, adaptable ropes, parachutes, and surface coatings are a couple of precedents of the conceivable approaches to use silk-based materials [80].

In view of its outstanding biocompatibility and biodegradability, silk has as of late pulled in impressive consideration as far as conceivable biomedical applications. Both regular and recombinant silk can be processed into different morphological structures, for example, films, wipes, nonwoven mats, hydrogels, platforms, and encapsulants. Silk has demonstrated to be a helpful biomaterial for the development of matrices for tissue designing and as a transport system of medications, nucleic acids, and proteins. It has been utilized as the suture material as a result of its higher elasticity and bioresorbable properties [76, 80, 96]. Silks with the best monetary significance are *Bombyx mori (B. mori)* silkworms that create covers from silk composite filaments to shield them from predators amid their transformation into moths. Web-weaving spiders (e.g., *Araneus diadematus or Nephila clavipes*) create various distinctive silk composite strands to catch prey (in networks), to defend their offspring/prey, and as lifesavers to escape from predators [7].

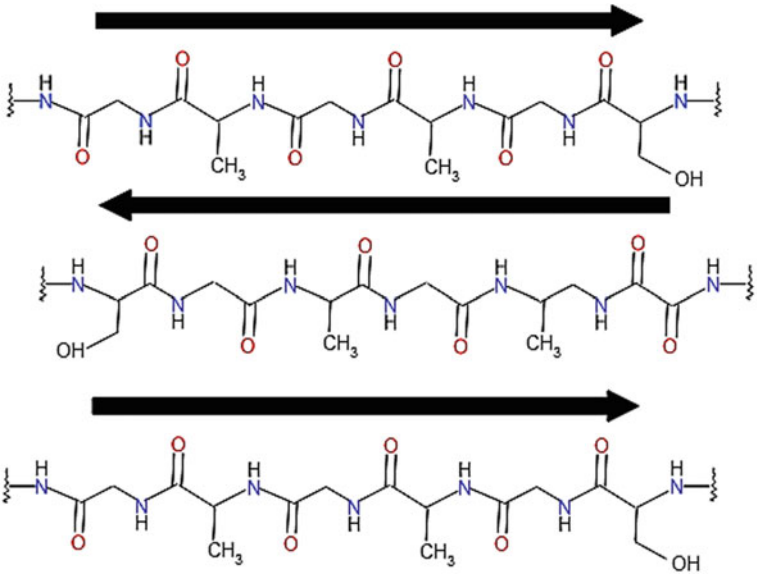

Fig. 11 Silk is fundamentally made out of (Gly-Ala-Gly-Ala-Gly-Ser)6 amino acid recurrent units

Silk Fibroin

Silk fibroin (SF) is the major basic protein of silk strands, and sericin is the water-dissolvable paste like protein that binds the fibroin strands together which is gotten after the extraction of sericin proteins from silk. SF strands are about 10–25 mm in width, and a single cocoon of silkworm, for example, Bombyx mori, may give more than 1000 m of SF strands. Silk fibroin has RGD (arginine–glycine–aspartic acid) grouping, which improves cell attachment, cell multiplication, and separation [7, 31, 96]. Fibroins found in silk strands, on account of *B. mori* silkworms, involve an overwhelming and a light chain (connected by disulfide bonds) and a little glycoprotein known as P25, which is related through non-covalent hydrophobic interactions. Two fibroin strands (known as brins) are covered with sericins, which are glue-like glycoproteins with differing molecular mass. *B. mori* silkworm silk can be created on an extensive scale by the training of silkworms. Silkworm cases are made for the most part out of two fibroin proteins covered with highly adhesive sericins, which are in charge of the strength of the cocoon structure [7, 31, 96].

Sericins can be separated from cocoons amid a thermochemical procedure called degumming. Extracting sericins is critical in light of the fact that the blend of silk fibroin and sericins can instigate immunological reactions. SF is one of the most grounded normal strands, and this quality can be ascribed to the synthetic structure of the protein itself. The amino acid arrangement of SF contains repetitive glycine–alanine–glycine–alanine–glycine–serine (GAGAGS) repeats which self-gather into an antiparallel b-sheet structure. These b-sheets are very crystalline and basically cross-link the protein through solid intermolecular hydrogen bonds and also solid van der

Waals associations between stacked b-sheets, giving the material strong mechanical properties [7, 31, 80, 96, 152]. Benefits of utilizing SF in biomedical applications comprise of the superb mechanical properties, moderate degradation profile, and fluid processibility. The degree of b-sheet structure can be controlled through physical or chemical technique, prompting materials with controlled crystallinity and degradation rate. The crystalline, hydrophobic b-sheet spaces keep the entrance of water and proteases bringing about moderate biodegradation of silk in vivo [31]. Crude and recovered version of SF have been widely utilized in biomedical applications, for example, sutures, coatings for cell culture, and 3D platforms for tendon, bone, ligament, and fat [7].

2.3 Polyester-based Biopolymers

Polylactic Acid (PLA)

PLA is a sort of direct aliphatic polyester got from inexhaustible resources, for example, corn, sugar, potato, and other farming items, whose properties are controlled by numerous factors, for example, the component isomers, getting ready temperature, and subatomic weight [7]. Lactic acid was first created by aging of a starch feedstock, for example, corn starch by soil microbes, and is then removed and polymerized. PLA, otherwise called poly(lactide), is created financially by ring-opening polymerization of the lactide, which is a cyclic dimer made out of two lactic acid units. Lactic acid contains asymmetric carbon molecule and as a result exists in two optically dynamic isomers (D and L). Thus, three optically isomeric types of lactide are conceivable: L-lactide (a dimer of L-lactic acid), D-lactide (a dimer of D-lactic acid), and mesolactide (a dimer of L- and D-lactic acid). The cycle of PLA in nature is presented in Fig. 12.

Generally, in view of various microstructural morphologies, the three types of PLA, poly(D-lactic corrosive) (PDLA), poly(L-lactic acid) (PLLA), and the racemic mix D, L-PLA (PDLLA) are semicrystalline with marginally extraordinary glass change temperatures, while D-PLA (PDLA) is constantly amorphous. The level of crystallization, and in addition the reactivity of polymer, is delicate to the proportion of D to L enantiomers utilized. L-lactic acid or D-lactic acid are acquired, based on the microbial strain utilized amid the fermentation process. High subatomic mass poly(lactic acid) is acquired either by the polycondensation of lactic acid or by ring-opening polymerization of the cyclic dimer 2,6-dimethyl-1,4-dioxane-2,5-dione generally alluded as dilactide or lactide [7, 31, 152]. PLLA is an adaptable, semicrystalline, degradable polymer having incredible mechanical properties, great biocompatibility, low poisonous quality, quick inexhaustibility, simple processability, and energy sparing possibilities. PLA is gotten from sustainable and biodegradable assets, for example, corn starch, potato, and rice, which can help lighten the vitality emergency and in addition lessen the reliance on petroleum products of our general public. PLA and its debasement items, to be specific H_2O and CO_2, are neither poisonous nor cancerous to the human body, subsequently making it an

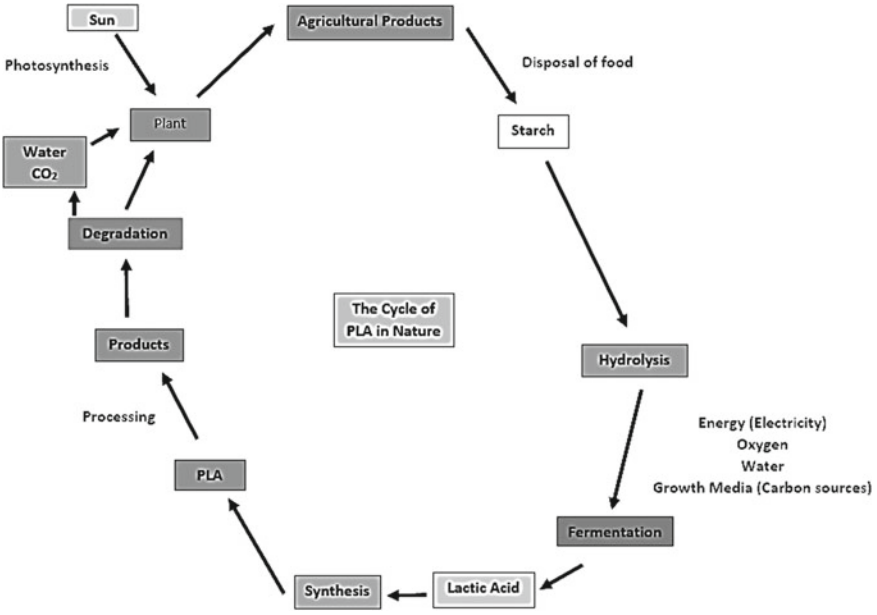

Fig. 12 Cycle of PLA in nature

incredible material for biomedical applications including sutures, clasps, and drug delivery system (DDS) [58]. Moreover, PLA can be manufactured by film casting, extrusion, blow molding, and fiber spinning because of its more prominent thermal processability in contrast to different biomaterials, for example, poly(ethylene glycol) (PEG), poly(hydroxyalkanoates) (PHAs), and poly(ϵ-caprolactone) (PCL). These thermal properties add to the utilization of PLA in the industry in fields, for example, materials and food packaging. PLA production expends 25–55% less fossil vitality than oil-based polymers. Cargill Dow has even focused on a decrease in fossil vitality utilization by over 90% when contrasted with any of the oil-based polymers for the not so distant future, which will without a doubt additionally prompt noteworthy decreases in air and water contamination discharges. It is a biodegradable thermoplastic with good mechanical strength and excellent biocompatibility. Being a thermoplastic and biodegradable, PLA has become attractive material for biological and medical applications [21, 31, 58, 152].

Polyhydroxyalkanoates

Polyhydroxyalkanoates are biopolyesters with different side chains and unsaturated fats with hydroxyl groups at the fourth or fifth position. They comprise of (R)-3-hydroxy unsaturated fats. There are three kinds of polyhydroxyalkanoates; short chain length hydroxyalkanoic acids (PHASCL) with an alkyl side chain, created by Ralstonia eutropha and numerous other microbes, PHASCL contain 3–5 carbon atoms, for example, poly-3-hydroxybutyrate (P3HB), poly-4-hydroxybutyrate

(P4HB), the second kind is medium chain length hydroxyalkanoic (PHAMCL) with alkyl side chains, produced by *Pseudomonas oleovorans* and other *Pseudomonas sensu stricto* [113, 116, 121, 127], PHAMCL contain 6–14 carbon particles and long chain length (PHALCL) acquired from long-chain unsaturated fats, which contain excess of 14 carbon atoms. The monomer composition, macromolecular structure, and physical substance properties of PHAs fluctuate, depending on the producer organism and in addition to the carbon source utilized for the development. PHAs containing twofold bond can likewise be developed by recombinant Methylobacterium extorquens strains when bolstered unsaturated fats [116, 141]. PHAs happen normally in an assortment of creatures, yet microorganisms can be utilized to tailor their generation in cells. The third kind is Polyhydroxybutyrate (PHB), the easiest PHA, was found in 1926 by Maurice Lemoigne as a constituent of the bacterium *Bacillus megaterium* [113, 116, 141]. PHB is collected in intracellular granules by a wide assortment of gram-positive and gram-negative living beings under states of a supplement restriction other than the carbon source. PHB contains repeating units of (R)-3HB. Polymerization of these polymers yields a high-molecular-weight polymer at a range of 200,000 to 3,000,000 Da, and it depends on microorganisms and their growth conditions. Polyhydroxyalkanoates (PHAs) belong to a class of bioderived polyesters. PHAs are utilized extensively in the biomedical field in view of their biocompatibility and controlled degradation rates. PHAs are appropriate for the fixing of delicate tissue and augmentation in creatures [63, 113, 116, 127, 141].

3 Biomaterials

Biomaterial or biomedical materials are characterized as material proposed to interface with natural frameworks to assess, treat, increase, or supplant any tissue, organ, or capacity of the body [2, 98]. Biomaterials as inserts and therapeutic gadgets are broadly used to supplant as well as re-establish the capacity of damaged tissues or organs, to help with recuperating, to enhance work, and to rectify anomalies, and this enhances the personal satisfaction of the patients. Biomaterials are materials of characteristic or man-made inception that are utilized to direct, supplement, or supplant the elements of living tissues in the human body [24, 115]. The utilization of biomaterials goes back to antiquated civic establishments [147]. Synthetic eyes, ears, teeth, and nose are found on Egyptian mummies [115]. It has been documented by researchers that the Chinese and Indians utilized waxes, pastes, and tissues in reproducing damaged or imperfect parts of the body. Throughout the hundreds of years, headways in manufactured materials, careful systems, and disinfection strategies have allowed the utilization of biomaterials from multiple points of view. Medicinal practice today uses various devices and inserts. For any of the polymer materials to qualify as a biomaterial, it must meet the biocompatibility requirement. This is the capacity of such material to work with the proper reaction from the host in a particular application.

All polymers considered for biomedical uses can be grouped into two general classes to be specific: normally occurring bioplastics and synthetic plastics [106]. The naturally occurring biopolymers include collagen, chitosan, alginate, fibrin, albumin, chondroitin sulfate, and naturally occurring poly(amino acids). They are excellent materials for biomedical purposes. They degrade well and are so highly suitable for temporary scaffold preparation for the repair of defected sites. However, the neat polymer lacks the required mechanical strength, hence the need to compound them. Figueirdo et al. [38] prepared and characterized 3D chitosan fragments for orthopedic applications by the addition of plasticizer as part of the formulation. Their aim was to enhance the delicate structure of chitosan-based materials. The results obtained revealed that chitosan with glycerol has prevalent mechanical properties and great natural conduct, in this way making the chitosan-gelatin-glycerol-based formulation a decent possibility to enhance chitosan composites for the development of bio-absorbable orthopedic insert. Qui et al. [112] described a methodology on the most proficient method to process bioceramic microparticle with poly(diol citrates) into bioceramic–elastomer composites for possible application in orthopedic implants. Their strategy comprises of a biodegradable elastomer poly(1,8-octanediol citrate) (POC) and a bioceramic hydroxyapatite (HA). Their work was aimed at assessing the viability of fabrication tissue fixation device utilizing machining and shaping systems. Their results revealed that exposure of the prepared composites to stimulated body liquid brought about broad mineralization as calcium phosphate with Ca/P of 1.5–1.7, like natural bone. The outcomes likewise uncovered that the composites supported osteoblast bond in vitro and the mechanical properties are appropriate for the manufacture of conceivably osteoconductive bone screws particularly the composites with 65 wt.% HA. Similar research work was carried out using poly(l-lactide) (PLLA), and the results had similar trends [146, 153].

The synthesized biopolymers include polyetheretherketone (PEEK), poly(hydroxyalkanoates) (PHA), poly (α-hydroxy acids) (poly(glycolic acid)), poly(lactic acid), poly(caprolactone) (PCL), poly(urethanes), poly(propylene fumarate, poly(orthoester), poly(anhydrides), poly(glycerol sebacate), poly(dioxanone), poly(phosphazenes), and poly(ethylene glycol). They have varying degrees of biodegradation [106]. Some have good water absorption capacity and some resistance to chemical attack. However, researchers have been able to blend a good number of these polymers to tailor their biomedical properties [37, 46, 57, 129, 154]. Furthermore, most of them have been compounded with different types of the naturally occurring biopolymer to give composites of excellent biomedical properties for orthopedic application [49, 59, 62, 152, 159]. PLA has been broadly examined for use in medicinal applications on account of its bioresorbability and biocompatible properties in the human body. The fundamental detailed models of restorative or biomedical items are bone fracture fixation gadgets like screws, sutures, conveyance frameworks, and miniaturized scale titration plates [33, 131]. PLA-based materials are created for the generation of screws and plates. As the bone healing advances, it is alluring that the bone is exposed to a steady increment in stress, along these lines decreasing the pressure protecting impact. This is conceivable just if the plate loses inflexibility in an in vivo condition. To address

this issue, analysts presented resorbable polymers for bone plate applications. PLA resorbs or debases upon implantation into the body; however, a large portion of its mechanical properties are lost within fourteen days [13, 40, 115]. Tormala et al. [137] proposed completely resorbable composites by fortifying matrices with resorbable PLLA strands and calcium phosphate-based glass filaments. One of the focal points regularly cited for resorbable composite prostheses is that they do not need to be removed by second operation, similarly as with metallic or non-resorbable composite inserts. To enhance the mechanical properties, PLA is strengthened with an assortment of non-resorbable materials [13].

4 Applications of Nanostructured Green Biopolymer Composites

Biopolymer composites have gained increased application in all areas of human endeavour. They are used in the industries such as food, medicals, electronics, and education. This is due to their ability to be degraded by microbes in the environment, leaving no harmful or toxic chemical behind. For nanostructured green biopolymer composites (NGBPC) that have some percentage of the synthetic polymer as part of their matrices, the breaking down of the whole material makes the fraction of the matrix left negligible.

The use and application of nanostructured polymer composites have increased tremendously in the last two decades from simple packaging application in almost every industry to very complex or delicate ones as in aerospace and medical applications. In all these, it is the design properties of the nanostructured biopolymer composites that determine its type of application. Many of the present-day nanostructured biopolymer composites are designed to resist heat exchange as in thermal insulators; reduce energy requirement as in automobile and aerospace industries; eliminate environmental or health-related problems as in degradable packaging; or just reduce the overall cost of the material. The end use is always factored into the initial design right from the start.

Many petroleum-based polymers are converted to biopolymer by compounding them with a suitable natural polymer, natural fibers, or nanoparticle, thereby widening their possible areas of application. Biopolymers such as poly(3-hydroxyalkanoates) (PHAs), polylactic acid, poly-epsilon-caprolactone have been modified in the past to suit selected biological application [140, 167].

Nanostructured biocomposites generally show enhanced properties, for example, mechanical moduli, thermal stability, great gas boundary, and biodegradability. Polymer/normal fiber composites have indicated expanded elastic modulus and diminished rigidity when contrasted with the pristine polymer. These behaviors have been credited to influences such as the fragile contact between the polymer, which is water-repellent in nature also, and the common fibers, which are hydrophilic [2]. The same behavior may also have contributed to the increased degradation rate of

these biocomposites. However, to overcome these problems, with the end goal to reduce the detrimental impact on the overall properties of the material, some forms of surface modification can be done [68].

Biopolymer surface properties are very vital in deciding its applications. The nearness of particular substance functionalities, hydrophilicity, unpleasantness, surface vitality, and geology is significant for biomedical utilization of PLA and its communications with bio-macromolecules. There is a need to structure biomaterials with the required surface properties. The distinctive surface change procedures incorporate a surface coating, entrapment, and plasma treatment. These are named physical strategies for surface change [152].

Cronin et al. [29] reported expanded cell connection to PLA fiber framework covered with extracellular lattice gel, fibronectin, and laminin when contrasted with the uncoated PLA film. Lu et al. [89], described surface-entrapment method as a basic and successful strategy for changing PLA surface and don't requires particular functional groups in the material. In addition, it does not change the mass properties of the material. Moreover, it tends to be utilized to create diverse morphologies and thickness of 30 frameworks, which is not conceivable with different techniques for surface change [168]. Plasma treatment can be utilized to present functional groups on the surface of PLA. In spite of the fact that this may influence the molecular weight of the polymer at first glance, it can enhance compatibility between the composite and the cell environment [27, 28, 52, 87].

5 Application of NGBPC in medicine

Nanomaterials offer promising new alternatives because of their similarity in dimension to the components of natural tissues. It is a known fact that the human body is governed by nanoscale events including the production of tissues. Therefore, it is believed that modification of biomedical materials to possess nanoscale features will definitely perform an important function in the production of a new-generation orthopedic materials [19].

Nanostructured biopolymer composites have been considered as the top-notch for tissue recovery. This is because they give an appropriate matrix condition, incorporate attractive organic properties, and show enhanced mechanical properties and controlled biodegradability [60, 69, 150]. Some researchers [122, 163, 164] have carried out a lot of investigations on chitosan–calcium phosphate composites for molding it into a permeable structure that allows osteoconduction. Zhang and Zhang [165] also developed a chitosan sponge, which improved the strength of the ceramic phase through strengthening of the matrix and subsequently protected the osteoblast phenotype [162].

6 Green Biopolymers for Medical Implants

The human body is constantly vulnerable to various sorts of sicknesses, injury, and wounds. A healthy skeletal system keeps the body actively going; however, several kinds of bone diseases can develop. Common among these accidents are osteoarthritis, osteoporosis, and bone cancer. Furthermore, accidents are a leading cause of bone fracture [67]; therefore, to heal fracture especially when the fracture site is wide enough, doctors have had to obtain patient's own bone from the pelvic region and transfer to the injured part. Based on the bigger threat for the patient and the cost implication, synthetic bone substitute opened extensive prospect for biocompatible materials to replace, treat, or manage medical problems associated with bone. Among the options available, nanocomposite offers a wider range for bone treatment. As defined earlier, the nanostructured composite is a heterogeneous blend of at least two materials, in which no less than one of the materials utilized must be on a nanometer scale. [25].

Before now, conventional materials like metals, ceramics, and manufactured polymers have been utilized as restorative inserts [117]. However, due to the problems of immunological rejection and poor biocompatibility, there was a need for researchers to look for better alternatives [90, 102, 120]. Biopolymers have been built up, as an auspicious class of materials with medical applications, non-cytotoxicity, biocompatibility, and biodegradation which made them an excellent choice for medical implantable materials. Probably, the most utilized body inserts comprise the heart, bones, eyes, ears, knees, and hips [22]. Most biopolymers biodegrade in the body without producing immunogenic materials [12, 100, 104, 118].

7 Orthopedic Application of NGBPC

The ability of nanostructured polymers in managing the conduct of bone cells (comprising bond, development, arrangement, and stretching) and, along these lines, advancing bone development, and recovery has been convincingly illustrated. The improving impact of nanostructured polymers with surface element sizes going from tens to several nanometers on osteoblast (bone-framing cell) reactions has been entrenched by an incredible number of studies [18, 85, 156, 160]. In light of these investigations, artificial and natural polymers (e.g., PLA, polyglycolic acid (PGA), PLGA, PCL, PU, gelatin, collagen, chitosan, and silk) have been built into nanostructures with satisfactory auxiliary properties to expand osteoconduction and osseointegration [156]. The topography, surface science, and wettability are a portion of the critical components that impact the conduct of nanostructured materials for orthopedic applications. Researchers have extensively investigated these factors [10, 26, 65, 83]. An in-situ polymerized biodegradable copolyester and hydroxyapatite were reported by [140], and the nanocomposites synthesized were mechanically ideal, bioactive, and biodegradable for conceivable orthopedic applications. Biodegradable

nanostructured materials have been utilized in orthopedic and other tissue designing and regeneration because of their one of the kind wetting and adhesive properties. The nanostructured materials can imitate the intricacies of extracellular matrix [54, 107, 126, 134]. The biopolymer nanostructural material also promotes osteogenic differentiation for different types of cells [54, 55, 144, 149].

Ma and Zhang [91] and Wei and Ma [146] prepared nanofibrous scaffolds using thermally initiated phase separation technique for biomedical application as scaffolds. In spite of the fact that the scaffold structure was controlled by fluctuating the weight proportion of the considerable number of components utilized, they were found to provide the biomimetic cellular environment. This expedited the propagation of numerous forms of cells [55, 145, 149, 153].

Many biopolymer matrixes have been reported in published works with good biomedical properties. However, the mechanical properties reported are not good enough for use in orthopedic applications [41, 61, 109]. Li et al. [81] prepared biopolymer composite films of MPEG-g-chitosan and methoxy poly(ethylene glycol)-b-poly(caprolactone) using casting/solvent evaporation method. From the characterization of the prepared films, it was observed that the chemical composition of the films had a strong impact on the thermal properties, morphology, water absorption, and in vitro degradation of the film. Furthermore, a change in the solvent used for preparing the biopolymer composite film showed no cytotoxic effect after 24 hours incubation [82]. Zhang et al. [161] developed nanocomposites of PLA/octadecylamine functionalized nanodiamond for use in tissue engineering. The report enhanced mechanical properties when contrasted with PLA, because of the enhanced proclivity observed between the polymer and the nanoparticles in the composites. The non-cytotoxicity and good biocompatibility observed indicate their possible applicability for tissue engineering.

Zhijianga et al. [166] prepared biopolymer composites for tissue engineering applications using poly(3-hydroxybutyrate-co-4-hydroxybutyrate) and cellulose as starting materials. The biocomposites were prepared by a freeze-drying method using trifluoroacetic acid as co-solvent. The prepared biopolymer composites were found to have better biocompatibility when compared to pure poly(3-hydroxybutyrate-co-4-hydroxybutyrate) scaffolds. The biopolymer composites were observed to form good cell adhesion and proliferation within 48 hrs when incubation test was done. This is, in addition to, having good mechanical property. The improved properties observed were attributed to the addition of bacterial modified cellulose to the biopolymer matrix. The pure matrix was reported to be brittle and hydrophobic [73]. However, the introduction of modified cellulose helped improve the biopolymer after absorption properties, leading to a good cell adhesion.

Bacterial cellulose (BC) varies from plant cellulose regarding its high crystallinity, ultra-fine system structure, high hydrophilicity, high mechanical properties, and biocompatibility [34, 71]. It has been modified to remove the lignin, hemicellulose, pectin, and wax in the original plant cellulose using microorganisms. BC has for quite some time been utilized in several applications, for example, diaphragms in speakers and headphones [56], papermaking [51] membranes [136], and electroconductive carbon film [158]. Inferable from its biocompatibility, BC has likewise

as of late pulled in a lot of consideration for biomedical applications. For example, BC has been effectively utilized as a synthetic skin for burn or wound recuperating material [6, 30, 78], synthetic veins for microsurgery [79]. The capability of BC framework for in vitro and in vivo tissue recovery likewise keeps on being investigated and indicates incredible guarantee [16, 48].

Ema et al. [35] developed cell structure of polylactide-based nanocomposites by means of a cluster procedure in an autoclave. Utilizing superficial carbon dioxide (CO_2) as a foaming agent, unreinforced polylactide and two distinct PLA-based nanocomposites were developed. The inclusion of nano-earth was accounted for to instigate heterogenous nucleation as uncovered by the portrayal of the interfacial strain between the matrix and the bubble.

Ji et al. [61] fabricated 30 biopolymers using gas-foaming technique from poly-DL-lactide/polyethylene glycol to be used for scaffolds. The thought was to enhance the retention and cell multiplication characteristics of biomedical material. The proportion of the polymer mixing demonstrated that the mechanical properties of PDLLA/PEG mix with under 30 wt. % PEG were reasonable for the manufacture of permeable scaffold. The pore size diameter achieved by the gas-foaming method was observed for an average between 15 and 150 nm. The 3D material had an average porosity of 84% on average making it a suitable material for the orthopedic application. However, compounding such material with any of the nanocellulosic materials like nanofiber, nanocrystals, and nanorod can greatly improve the observed properties [5, 86]. This is because the literature has confirmed that nanocellulosic materials have good compatibility and their degradation is with no immunogene [84, 105].

8 Conclusion

Nanostructured green biopolymer composites have been defined as biodegradable polymer composites with nanostructured particles/fibers, present inside the composites. Although biopolymers are originally termed polymers found in nature (natural polymers), many research works have shown that blending synthetic polymers with a biopolymer or compounding synthetic polymer matrixes with natural fibers can introduce biopolymer properties onto the new materials, thereby widening their areas of possible applications. Nanostructured materials have shown great improvement in their mechanical, thermal, optical, and gas obstruction properties as a result of their increased surface areas. These have also helped to widen further their possible areas of applications. The presence of nanostructured particles in biopolymer composites for medical applications, especially for orthopedic applications, has made it possible and easier for such material to mimic the body nanostructured bio-macromolecule. The competency of nanostructured biopolymer composites in controlling the conduct of bone cells and promoting their development and regeneration has been demonstrated convincingly, in many research works. In addition, gradual and regulated degradation of the nanostructured biopolymer composites and the gradual transfer of stress to the newly formed bone tissues make this group of biomaterials excellent.

This is in addition to the fact that they do not produce immunogenic substances and most times do not require the second open surgery unlike other types of biomedical for orthopedic applications. Truly, the future of biomedical materials for orthopedic applications is in nanostructured biopolymer composites. The composites can be tailored to meet any functional requirement by simply changing their compositions or varying their ratio of compounding.

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Chapter 8
Bionanopolymers for Drug Delivery

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1 Introduction

In medicine, the need and demand for the successful delivery of pharmacologically active materials or therapeutic compounds to cells, tissues, and organs in the system have made drug delivery techniques broadly studied. Several drug delivery methods have been developed and investigated in the past [180]. The aim is to design better approaches to treat various diseases affecting humans in the world. This has led to the development and use of different materials of natural and synthetic origin as drug delivery devices. However, certain limitations and challenges have been faced with the use of most of these materials hence the need for more suitable alternatives. Some of these limitations include material toxicity, non-biocompatibility, and

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non-flexibility among others. At the moment, research has brought to limelight some group of materials with unique properties that can potentially serve as drug delivery systems. They are commonly referred to as biopolymers and because they can be manipulated, they can be fabricated into nanosizes (sizes of between 1 and 100 nm); hence, they are called bionanopolymers. Bionanopolymers are generally of natural origin, they are biodegradable and biocompatible. These properties have made them widely employed in biomedical applications [178]. Bionanopolymers have gained attention in drug delivery [84, 143] and have contributed to the progress recorded in the treatment of disease conditions such as cancer [25], diabetes [13], allergy [166], infection [57], and inflammation [214]. They are known to increase the therapeutic effect of drugs at the same time minimize the side effect. Their flexibility permits the engineering of plenty of functionalities needed for delivering drugs efficiently, at the same time, maintaining biocompatibility, facile manufacturing, and formulation stability [29]. A lot of reasons account for their use in a therapeutic application; these include similarity in domain size as proteins, a large surface area which allows the display of a large number of functional groups. In addition, their high abilities of diffusion and volume change provide rapid absorption and good release behavior [138]. Another great benefit associated with the use of bionanopolymers is the ability to tailor or control their particle size and surface characteristics. For example, the surface characteristic can be modified by binding the surface to the functional molecule covalently and assembling them layer-by-layer [223]. Low drug-loading, wide size distribution, and difficulty in scaling up are some limitations of these biomaterials. These, however, have not affected the interest chemists, biologist, and pharmaceutical scientist have in them. This is because they are promising drug delivery vehicles for transporting bioactive agents to several parts of the body compared to other materials [71, 220].

This chapter thus focuses on the utilization of commonly used biopolymers such as proteins (with emphasis on collagen), polysaccharides (with emphasis on chitosan), and polyester (with emphasis on polyhydroxyalkanoates (PHAs)). Their structures, synthesis, and application as biomaterials in biomedicine for drug delivery are discussed.

2 Drug Delivery Systems

For a successful and efficient management of diseases, a valuable therapeutic approach is of great importance. Therefore, a drug delivery system must be one that permits the introduction of therapeutic agents into the body in order to improve the drug's efficacy. Also, the safety, time, and mode of delivery of any drug delivery system should be considered at the experimental or clinical level [197, 199]. The aim of every drug delivery system is to localize administered pharmacological agent at a selectively targeted site in the body at a controlled rate with reduced side effects that may arise from systemic treatment. Research for this better alternate drug delivery system has been ongoing for over two decades and successes have been reported.

The development, study, and formulation of microsphere, nanomaterials, and hydrogels among others from biopolymers are rapidly becoming promising routes for drug delivery [176]. Generally, the delivery of drugs is achieved by using the chemical formulation of the drug, medical device, or both. Currently, various systems such as particulate carriers, polymer gels, and lipids are employed as drug delivery systems [10, 90, 135, 193, 194, 212]. Some properties that make a drug delivery suitable for delivering therapeutic agents in the body include nonimmunogenic, non-toxic, biocompatible, good biodegradability, controllable drug release, and ease of consistent reproducible and clinical-grade synthesis [76]. All the various types of drug delivery system that are used to deliver bioactive agents in different fields in medicine are grouped into two. These are conventional and the novel drug delivery system.

2.1 Conventional Drug Delivery System

This type of drug delivery system is referred to as traditional drug delivery system. It involves the delivery of pharmaceutical compounds into the body by using the common and usual methods. Common examples of this type of delivery system include oral delivery, transdermal delivery, and parenteral delivery such as buccal/sublingual delivery, rectal delivery, intravenous delivery, subcutaneous delivery, and intramuscular delivery among others. These individual delivery systems have their peculiar benefits [182].

2.1.1 Oral

The oral route of drug delivery remains the most popular drug delivery system. Drugs delivered via this route are often absorbed in the small intestine which provides 100 m^2 epithelia surface for drug transfer. However, if it is a drug that has poor solubility, absorption may also take place in the large intestine [70]. The advantages of this drug delivery system are (i) convenience of administration, (ii) non-invasive, (iii) accurate and measured dose, (iv) unit dosage form, (v) cheap for the patient, and (vi) reduced infection risk compared to subcutaneous injections [33, 217]. Disadvantages associated with this route of drug delivery are (i) cannot be used by unconscious patients, (ii) low solubility and permeability, (iii) degradation by gastrointestinal enzymes or flora, (iv) food interactions (v) quick clearance time of between 4 and 12 h, and (vi) irregular absorption [129, 107, 106], making this form of drug administration less effective.

2.1.2 Transdermal

Transdermal drug delivery system is one that is designed to deliver therapeutic agents in dosage form across the skin of patients [2]. This system is a discrete dosage form

that is otherwise known as patches [21, 95]. The first transdermal drug delivery system (Transderm SCOP) was approved by the food and drug administration in the year 1979. This was used to prevent nausea and vomiting when traveling. The major aim of this drug delivery system is to get drugs into the systemic circulation via the skin. This is done at a rate that is predetermined with slight inter- and intra-patients variation [95]. The design of several transdermal drug delivery systems is such that the therapeutic agent is released for a period of several hours to days upon application to the surface of the skin. The advantages this drug delivery system are reduction of workload placed on digestive tracts and liver by the oral route, patients comply more to drug administration and the harmful side effect of drugs as a result of a temporary overdose is minimized [2]. In addition, it permits the continuous addition of drugs that have a short half-life and also prevents pulsed entry of drugs into the system that most times lead to harmful side effects [95]. Other benefits of this drug delivery system include limited hepatic first-pass metabolism, the enhanced therapeutic efficacy of administered drugs, and ability to maintain a steady plasma level of the drug [77]. It has been found that this drug delivery system is beneficial for prophylactic therapy in chronic disease conditions [124]. By measuring the level of the drug in the blood, detecting the excretion of the drug and its metabolic products in the urine, the percutaneous absorption of the drug is evident. The clinical response of patients that were administered drugs through this route is also a valid way to ascertain the efficacy of this drug delivery system [77].

2.1.3 Parenteral

Parenteral drug delivery is simply any non-oral means of administering bioactive agents into the body. It is generally a method that injects therapeutic compounds directly into the body, bypassing the skin and mucous membranes. The common parenteral routes include intramuscular (IM), subcutaneous (SC), and intravenous (IV). Table 1 shows some of the advantages and disadvantages of the different parenteral drug delivery routes.

First-pass metabolism is a process whereby the concentration of the drug is reduced before it eventually arrives into the systemic circulation.

2.2 Novel Drug Delivery System

These classes of drug delivery system are those designed to continuously deliver drugs at predictable and reproducible kinetics over an extended period of time in the circulation. The major advantage of this type of drug delivery system is minimized side effect of the administered drug, controlled therapeutic blood level, and improved compliance by patients. This is because the frequency and total drug dosage are greatly reduced [11, 60]. This drug delivery system consists of three individual systems, viz. targeted, controlled, and sustained/modified release drug delivery sys-

tem. The ability to combine these systems further increases the therapeutic efficacy of drugs in disease management and treatment [206].

2.3 Targeted Drug Delivery System

It is a drug delivery system otherwise known as smart drug delivery system. It delivers drugs to patients in a manner that makes the drug available for a prolonged time period and in increased concentration in the targeted site compared to other body parts. As oppose conventional drug delivery systems, drugs are absorbed across a biological membrane and the therapeutic agent is released in dosage form at the site of the target. Advantages of this delivery system include a decrease in the frequency of ingesting the drug, reduced drug circulation fluctuations, reduced side effects, and required drug level in the plasma, and tissue is retainable thus prevents tissue damage. On the other hand, the disadvantages of this delivery system are limited dosage adjustment and the high cost of production. In addition, it is a system that cuts across different disciplines and requires the active collaboration of these disciplines in order

Table 1 Advantages and disadvantages of common parenteral drug delivery system [32, 205]

Type of parenteral route	Advantages	Disadvantages
Intramuscular delivery	Self-administration is possible by patients, more volume can be administered compared to subcutaneous, and it can bypass first pass metabolism	It is invasive (patient discomfort), irritating, and can cause inflammation
Subcutaneous delivery	Patient can self-administer the drug, complete absorption but slow and bypasses first-pass metabolism	It can be irritating, cause inflammation, and has a maximum dose volume
Intravenous delivery	Drug's bioavailability is 100%, induces rapid response, blood concentration can be controlled, it maximizes incorporation of degradable drugs and bypasses first pass metabolism	It is invasive, a trained personnel is required to administer the drug and there is the possibility of toxicity due to incorrect dosing and sterility
Sublingual delivery	It bypasses first-pass metabolism, rapid drug absorption, low activities on enzymes	There is discomfort during dissolution, the probability of swallowing loss of effect and small doses can only be administered
Rectal delivery	It can also bypass first-pass metabolism, and it is a good method to administer drugs to children	It can be degraded by bacterial flora, its absorption largely depends on the state of the disease, and it can be discomforting

to achieve the desired result. Factors to be considered before fully implementing a targeted drug delivery system are the drug properties, side effects of the drugs, the drug delivery route, the targeted site, and the disease to be treated [5, 119, 131, 210]. Due to the fact that the targeted drug delivery system seeks to improve the overall curative effect of the drug as well as reduced its toxicity, two approaches otherwise called classes of targeted drug delivery system are employed. These are

1. Passive targeting: This involves drug delivery via blood circulation. Drugs embedded in drug carrier systems are gathered at the particular site of the disease in the body. The action and release of the drug are limited to particular sites in the body. For example, an anticancer agent is targeted to the tumor site and not the liver. Although this requires the specific control of the size and surface of the delivery device to avoid uptake by other organs [64, 65, 159].
2. Active targeting: This takes place majorly after blood circulation and extravasations. It involves the interaction of specific type of ligand-receptor for intracellular localization. This form of targeting is further classified based on the different targeting levels.
    - First-order targeting: Here, the distribution of the drug carrier system is restricted to the capillary bed of a predetermined target site, organ, or tissue. For instance, targeting of compartments in lymphatics, peritoneal cavity, pleural cavity, cerebral ventricles and eyes and the joints [159].
    - Second-order targeting: In this case, specific site (cell type) is targeted for drug delivery. For example, tumor cell targeting rather than normal cell and selectively delivery drug to kupffer cells in the liver [4].
    - Third-order targeting: This involves the precise delivery of drugs to the intracellular site of the targeted cells. For example, receptor-based ligand-mediated entry of a drug complex into a cell by endocytosis [64, 81, 131].

2.4 Controlled Drug Delivery System

This is a system that involves a predesigned manner of delivery (releasing) drugs incorporated into drug delivery vehicles into the body system. Here, the concentration of the drug and the drug's pharmacokinetic characteristics are put into consideration and the drug is administered at a predetermined rate and time. Currently, drug delivery systems that are stimuli-responsive have gained attention for controlled release of drugs because they can be controlled easily and can be triggered externally. Such external factors include pH [36, 102] temperature [34, 97], ionic strength [175], and electric field [140]. The release of the therapeutic agent may occur at a constant or cyclic rate over a long period of time. However, the ultimate goal is to obtain a better therapeutic efficiency and avoiding under/overdose. Drug carrier capable of encapsulating drugs and releasing them at controlled rates (hours, days, weeks, and even months) is widely employed in this system. Advantages of this system include

tailored drug release rates, protection of fragile drugs, patient's compliance, and comfort.

2.5 Sustained Drug Delivery System

This form of drug delivery system is a modified form of administering drugs to patients. It can serve as a more efficient substitute to the conventional drug delivery system. This is achieved by sustaining the drug release and at the same time maintaining the concentration of the drug in the plasma. Sustained drug release system prevents peak and trough in dosing and a constant concentration of the drug is found available in the therapeutic window. Benefits associated with this delivery system are uniform drug delivery, low-dose frequency, increased drug effectiveness due to the localization of the drug, evasion of multiple dosing, little or no side effect, and ability to overcome challenges faced by conventional drug delivery system [96, 98, 148]. Physiochemical factors such as dose size, ionization, partition coefficient, drug stability, half-life, therapeutic index, absorption window, plasma concentration-response relationship, drug metabolism, pKa, and aqueous solubility are linked to the manner which drugs are administered through a sustained drug delivery system [17, 78, 152].

Although sustained drug delivery system and controlled drug delivery system are different drug delivery processes, they are usually mixed up in an inconsistent and confusing way because of the similarities in their processes. The major difference between them is that controlled release is a perfect zero-order release; that is, the drug is released over time irrespective of the drug's concentration. Whereas, the drug is slowly released over a period of time in sustained manner and it is not time dependent [20, 99]. It can either be controlled or uncontrolled [24, 105, 211].

3 Bionanopolymer

These are polymers obtained from natural origin (living organisms) during the growth cycles. They are synthesized by enzyme-catalyzed, chain growth polymerization reactions of activated monomers, which are typically formed within cells by complex metabolic processes [178]. They are non-toxic, less expensive, and easily available; therefore, they have been more greatly employed in the diverse application as delivery carriers of therapeutic drugs compared to synthetic polymers. However, for them to be used for this purpose, it is necessary for the particle size, charge, surface morphology, and drug release rate to be controlled [138]. They usually tailor-made as drug delivery devices in nano-sized forms, and this involves a various process of preparation. These macromolecular-based mucoadhesive biomaterials have been considered for several years and used as drug delivery vehicles and quite a number of successes have been reported [129]. With the use of these bionanopolymers as drug

carriers, many limitations (e.g. enzymatic degradation of drug) of the different drug delivery system has been overcome. For example, increased buccal penetration has been achieved using biopolymer micro-/nano-sphere formulation [75, 169]. Hence, they have been identified as protective agents against rapid drug degradation [107, 153, 186].

3.1 Types of Bionanopolymer

Bionanopolymers are divided into various groups; some of these groups are polysaccharides, proteins, and nucleic acids. Numerous examples of each class exist but for the purpose of this chapter, a representative member of each group will be emphasized and discussed in details. The focus is on collagen, chitosan, and polyhydroxyalkanoate (PHA) which are bionanopolymers of protein, polysaccharide, and polyester origin respectively.

3.1.1 Protein

Proteins are natural, thermoplastic heteropolymers polymers. They are made up of different polar and nonpolar α-amino acids, most proteins are not soluble nor fusible [31]. They have advantages such as biodegradability, low toxicity, high stability, and excellent binding capacity of diverse drugs [42, 62, 91, 209]. They are also able to emulsify, form gels and possess water-binding capacity [49, 50, 209. In addition, they show some drug-loading mechanisms such as electrostatic attractions, hydrophobic interactions, and covalent bonding [51]. Additionally, the presence of functional groups on the surface of nanoparticles makes modification possible thus permits specific drug targeting to the site of action [138]. These properties make them different from synthetic polymers and have made protein-based nanocarriers promising candidates for drug and gene delivery. Some of these proteins of natural origin have already been studied, designed, and used as biomaterials for drug delivery. Examples are collagen [55, 145], elastin [40] and fibronectin [44]. Currently, research has led to the development of genetically engineered protein with properties that can be manipulated. Therefore, more protein-based nanocarriers with better drug delivery properties are available for drug delivery applications. Collagen, which is the protein of interest in this chapter, is a natural protein that exists in the body as a major component of the extracellular matrix of animals [113]. The total body protein consists of between 25 and 35% collagen, and they are in the form of elongated fibrils. They are abundantly found in tissues such as bone, cartilage, tendons, blood vessels, ligament, skin, cornea, intervertebral disk, and the gut [149]. They are found within and outside the cells of the body. Collagen possesses excellent tensile strength and firmness to the tissues in the body [167]. Collagen exhibits superior biocompatibility compared with other polymers of natural sources, for example, albumin and gelatin [113]. When the medical application of biomaterials began to expand in the 1970s,

most research laboratories focused their studies on collagen. Since then, collagen of medical grade, improved processing technology became easier to obtain [137, 221, 222] and subsequently, collagen was employed as a drug delivery system. It has been in use for years as a biomaterial because of its biocompatibility, low antigenicity, and biodegradability [113]. At the moment, collagen is still one of the best biomaterials that have a broad range of application as a delivery vehicle for drugs, proteins, and genes. Thus far, it has been proven to function effectively in controlled release and localized drug delivery [125]. It has been used as a drug vehicle in ophthalmology, as injectable dispersions in cancer treatment, as sponges carrying antibiotics and as implantable mini-pellets loaded with protein drugs. However, the biological, physical, and chemical properties of collagen are still being studied in order to improve the overall properties, as well as overcome some of its limitations in the application as a drug carrier [83]. It is generally anticipated that collagen-based materials will become a useful matrix substance for biomedical application, especially in drug delivery.

3.1.2 Polysaccharide

Polysaccharides are a group of biopolymer of the natural source and have a number of advantages over synthetic polymers. They are non-toxic, can be produced at a relatively low cost, and are very biocompatible. Hence, they are promising ideal materials for the synthesis of drug delivery systems [45, 46]. Examples of polysaccharides include starch, cellulose, and chitosan among several others. However, the emphasis is on chitosan in this chapter. Chitosan is a linear polysaccharide that occurs naturally and one of the most abundant in the environment [12]. It is produced by chitin and found in only some species of fungi (*Mucoraceae*) [3]. Chitosan is a semi-crystalline polymer that is solid and exhibits a degree of polymorphism [141]. It is known to possess chemical activity thus, increasing its range of applications. Although the discovering of chitosan dates as far back as an early nineteenth century, it has only been used in biological applications and drug delivery systems (such as nanoparticle microspheres) in the last two decades [47]. It is one of the most widely studied and used marine polysaccharides for biomedical application. It has now become a great biomaterial of interest to the pharmaceutical industry in drug delivery and several publications on its use as a drug carrier has been seen [129]. Review on the biodegradation, biodistribution, and toxicity [86] as well as its formulation for DNA and siRNA [118] delivery has been considered. Its application as hydrogel for controlled, localized drug delivery [17]; nanostructures for delivery of ocular therapeutics [41] have also been reported. In addition, its use as a drug carrier for targeted delivery of low-molecular drugs have also been stated [146]. It is important to know that the mucoadhesive properties of chitosan play a key role in its usage in oral, nasal, and ocular drug delivery [68, 69, 74]. At the moment, chitosan is designed as nanoparticles, beads, and capsules for controlled drug delivery systems [3, 39, 154, 184]. The biological properties of chitosan make it an excellent candidate for applications that require contact with biological environments. Also,

these properties allows the incorporation and delivery of pharmacologically active substances [73, 183]. The electrostatic interaction between a chitosan-based drug delivery system and the bioactive compound is crucial to the drug's stability, protection and the ultimate release of the drug. In other words, a positively charged polymer like chitosan will be more suitable to deliver an anionic drug than a cationic drug [30].

3.1.3 Polyester

They are biodegradable polymers that are currently considered the most competitive for various applications in the biomedical field. They are biocompatible and their physicochemical properties make them suitable and ideal for a wide range of application in medicine [1, 43, 160]. Apart from being used as a drug delivery vehicle in controlled drug release system, medical devices are also manufactured from them [114, 134]. In drug delivery applications, they act as a biological inert support material like a mesh or drug carrier. There are different types of polyester in existence that are used in biomedicine. However, the most commonly employed are polylactic acid (PLA), poly(lactic-*co*-glycolic acid) (PLGA), poly(ε-caprolactone) (PCL), polyhydroxyalkanoate (PHA), e.g., poly-3-hydroxybutyrate (or poly-β-hydroxybutyric acid, PHB). Polyhydroxyalkanoates are a type of naturally occurring polyesters. Their discovery dates back as far as 1888 but was not called PHA by biochemists [161]. They have obtained from over 75 different bacteria genera both gram-positive and gram-negative bacteria. They are stored in the cytoplasm as granules and forms about 90% of the dry weight of the cell [26, 103, 112]. The molecular weight of PHA is between 50,000 and 1,000,000 Da depending on the type of bacteria it is obtained from. The monomers of PHA provide different types of materials with properties ranging from rigid and stiff to flexible and elastomeric, including polymers that degrade relatively quickly in vivo and others that are slow to degrade [72] . Typical examples of this class of polyester include Poly(3-hydroxybutyrate) P(3HB), Poly(3-hydroxyhexanoate), Poly(4-hydroxybutyrate), Poly(3-hydroxyoctanoate) P(3HO), Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate), Poly(3-hydroxyvalerate), Poly(3HHx-*co*-3HO) and Poly(3HB-*co*-3HV). Generally, the degradation of this group of polyester depends on the microbial activity of the environment, the surface they are exposed to, moisture, temperature, pH, molecular weight, polymer composition, crystallinity, and nature of the attached monomer unit of the PHA [23, 103, 189]. They are used as delivery vehicles for localized drug delivery with a controlled release of the entrapped compound over a period of time [104]. PHAs have excellent properties far beyond the synthetic polymers used in the biomedical application. Currently, these PHA are considered worthy of intense research for the possibility of modifying their properties in order for them to serve in more areas in medicine.

3.2 Structure and Synthesis

3.2.1 Collagen

The first and correct model of collagen structure was known as *Madras Model*. This model was proposed by Ramachandran and Kartha [170]. Collagen is made up of a triple helical structure that contains two homologous chains (α-1) and one supplementary chain with varying chemical composition (α-2) [167]. The triple helical structure of collagen is made up of three polypeptide a-chains with more than a thousand amino acids in each. The individual chains have a different turn in the reverse direction and they are linked together primarily by hydrogen bonds between nearby CO and NH groups. These various polypeptides present in collagen are made up of mainly proline, hydroxyproline, glycine, and lysine. Although, glycine makes the smallest side group, the quantity of the glycine present determines the degree of flexibility, the more the glycine content, the greater the flexibility of the collagen chain [61]. Glycine unit is repeated at every position on the sequence; thus, it permits the chains to be well closely packed, leaving very little core space for residues. Proline constitutes about 35% of the non-glycine positions in the Gly-X-Y sequence, but it is mostly found in the X-position while 4-hydroxyproline is found in the Y-position [83]. Hydroxyproline is a product of the posttranslation of proline, and it is mediated by the enzyme prolylhydroxylase [94]. This makes up about 10% of the amino acid present in collagen. Collagen also consists of unusual amino acid known as hydroxylysine, produced from lysine via enzymatic hydroxylation by lysyl hydroxylase enzyme. The formation of the unusual amino acid permits the sugar components to attach to the structure, to form the three helical collagen structures. Imino acids are also found in collagen, and they help to stabilize the triple helix structure. They also cause the A-chain and form hydrogen bonds that limit rotation [150]. There exists very little difference between collagen obtained from different species of vertebrates [196]. Generally, collagen molecule weighs 300 kda and its rope-shaped structure has a length and width of 300 and 1.5 nm, respectively [167].

The synthesis of collagen is made possible by fibroblast cells. The preliminary materials used to synthesize collagen used in biomedicine, especially drug delivery is obtained from human tissue that is rich in fibrous. For drug delivery purposes, four types of collagen are isolated and purified. These are natural salt-soluble collagen, alkali, and enzyme-treated collagen, acid-soluble collagen, and insoluble collagen. In addition, collagen of various types like procaine, bovine, and sheep can be derived from different sources such as marine sources, human placenta, and recombinant human collagen from transgenic animals [167].

3.2.2 Chitosan

Chitosan occurs naturally as linear polysaccharide produced by alkaline deacetylation and chitin [54]. It consists of amine groups that are sensitive to changes in pH.

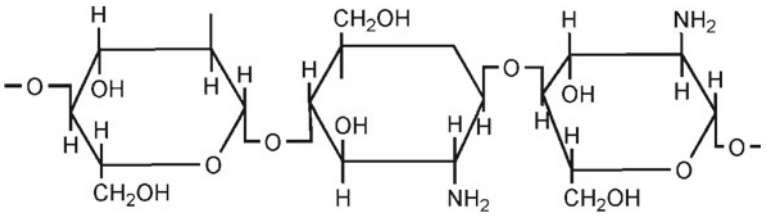

Fig. 1 Structure of chitosan

They are positively charged in an acidic medium but neutral in an alkaline medium [115]. The rigidity, compact crystallinity in structure and strong intra- and intermolecular hydrogen bonding makes chitosan insoluble in water and alkaline media [208]. Chitosan has a very amazing structure whose fundamental skeleton does not change despite any alteration made on the structure. The original physicochemical and biochemical properties are still maintained while possessing new and improved properties at the same time. Their wide application in pharmaceutics, biomedicine, and biotechnology is as a result of the broad range of derivatives available, each with its own unique properties [130]. Chitosan can be modified for various applications by oligomerization, alkylation, acylation, hydroxy alkylation, carboxy alkylation, sulfation, phosphorylation, enzymatic modifications [47]. The ability to modify chitosan is a good approach to increase the effectiveness of drug release, protection, and stability [6]. Chitosan has been reported to have a rigid rod-type structure [35, 52, 53, 82, 128, 195] or a semi-flexible-coil [15, 27, 100, 123, 171, 204, 207]. It has also been reported that the degree of flexibility (in terms of persistence length) is reasonably influenced by DA [123, 195]. Figure 1 shows the chemical structure of chitosan. The chemical structure is shown in Fig. 1.

As earlier stated, chitosan is synthesized by the deacetylation of chitin. This leads to the production of a compound having a D-glucosamine residue and N-acetyl-D-glucosamine which represents the deacetylated and acetylated unit, respectively. These residues are randomly distributed within the compound, but glucosamine units are known to be predominant [6, 162, 208]. The degree of deacetylation is dependent on the ratio of glucosamine to acetyl glucosamine; there are between the ranges of 30 and 100% [147]. The degree of acetylation of chitosan can vary from zero (full deacetylation) to one (full acetylation). This is made possible due to the ability to replace the N-acetyl group present in chitosan by NH_2 [129]. The acetylated and deacetylated monomers which are GlcNAc; A-unit and GlcN; D-unit, respectively, are either randomly distributed or distributed in a block-wise manner [201, 202]. Chitosan can be designed for drug delivery purposes using different techniques such as multiple emulsion, solvent evaporation, coating deposition, and successive bark chitosan [109].

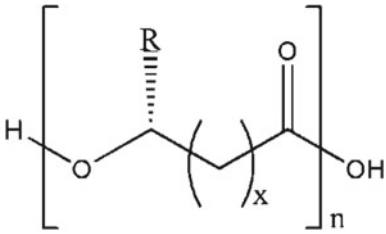

Fig. 2 Generic structure of PHAs

3.2.3 PHA

PHAs are biodegradable, hydrophobic, and crystalline biopolymer that has gained increasing interest among other class of biodegradable biopolymers. PHAs are a class of polyester, accumulated in the granules of different bacterial cells as energy storage material under growth conditions that are not balanced [180]. They are often modified to take care of problems such as low cell adhesion, hydrophobicity, and inflammatory side effects associated with the use of some synthetic polymers [173, 93]. PHA consists of over 100 types of hydroxyl acid monomers, the monomers units of hydroxyalkanoate ranges from 2- to 6-hydroxy acids. These monomers can be substituted with a broad range of side groups such as alkyl, aryl, alkenyl, halogen, cyano, epoxy, ether, acyl, ester, and acid groups [190]. These monomers help provide additional structural properties to the polymer [72]. They are grouped into short chain length (SCL) and medium chain length (MCL) consisting of 3–5 carbon atoms and 6–14 carbon atoms, respectively. They consist of only chirally pure (R)-configuration monomers [180]. Even though they are of biological origin, they have few resemblances in structure to synthetic polymers used in medical applications [47]. The general structure of PHA is shown in Fig. 2.

PHAs are generally synthesized by different gram-positive and gram-negative bacteria such as *Azotobacter* sp., *Pseudomonas* sp., *Bacillus* sp., and *Methylobacterium* sp. [188]. PHA synthesis is achieved by the metabolic biosynthesis of PHAs molecules by these microorganisms when there is excess carbon but limited nutrient [87, 189]. Most PHAs are synthesized by metabolic biosynthesis, and this pathway has been studied. For example, the metabolic pathway that leads to the synthesis of PHB involves the formation of a carbon–carbon bond of two acetyl-CoA moieties by the action of β-ketothiolase. 3-hydroxybutyryl-CoA is further formed by the reduction of acetoacetyl-CoA by the enzyme NADPH-dependent acetoacetyl-CoA reductase [88]. PHB, an example of PHA is synthesized by the polymerization of (R)-3-hydroxybutyryl-CoA molecules by the PHB synthase thus, the formation of PHB granules [151]. The synthesis of PHA is dependent on the NADH to NAD+ ratio, an increased NADH/NAD+ ratio is observed when the nitrogen source is finished. This inhibits the action of the enzyme β-ketothiolase, thus preventing the entering of Acetyl-CoA into the PHA biosynthetic pathway to produce 3HB monomers [7, 139]. The most bacteria strain used for the industrial production of poly-(R)-3- hydroxybutyrate (PHB), poly((R)-3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB),

and poly((R)-3-hydroxybutyrate-*co*-(R)-3-hydroxyvalerate) (PHBV) is *Cupriavidus necator*. Generally, PHA that is synthesized in vivo is of high-molecular weights. Recently, synthesis of PHA from plant origin for biomedical application is increasingly considered and investigated [180].

4 Biodegradation

Biodegradable polymers generally have labile bonds in their backbones that can be hydrolytically or proteolytically degraded [187]. One property that makes bionanopolymers unique is their ability to degrade in the different environment. They degrade within the body due to natural biological processes, thus when used as a drug delivery system, it eliminates the need to remove them from the body system [58]. Most often, they degrade by a process known as hydrolysis, into smaller compounds or molecules that are biologically acceptable by the body hence their broad application in biomedicine [177]. For example, PHAs can be broken down completely into water and carbon dioxide by a lot of microorganisms present in the soil, water, and sewage environment [28]. Some bacteria and fungi are known to excrete enzymes capable of degrading solid PHAs into water-soluble monomers and oligomers which are subsequently used as nutrients within the cells [180]. Chitosan is degradable by enzymes such as chitosanase or lysozymes, hence their wide application in biomedicine [133]. The stability/degradability of chitosan is crucial to the pharmaceutical industry because it plays a vital role in the function of chitosan in different formulations [132, 185]. Factors such as temperature are also considered in the storage of chitosan as this may cause depolymerization. Depolymerization may be detrimental to the purposed application based on the significant functional changes that occur [127, 136]. The degree of deacetylation of chitosan is also a parameter that can be used to control the rate of its degradation [3, 19]. Collagen, on the other hand, degrades by denaturation in most cases; however, this can be coupled with physical and/or chemical processes. This results into the production of a polypeptide with high-molecular weight known as gelatine. This protein (gelatine) is further degraded by the enzyme proteases by the hydrolysis of the amine functional group that is present [31].

5 Formulations of Bionanopolymers for Drug Delivery

The use of bionanopolymers as drug carriers for various drug delivery systems in the treatment of several diseases is currently been studied in depth [178]. For this to be successfully achieved, these bionaopolymers are formulated to suit the particular application. These formulations can either be capsules, gels, nanoparticles, tablets, etc. The main reason behind this specific design of bionanopolymer is to adequately protect certain therapeutic agents that degrade or metabolize rapidly as soon

as they are administered [58]. This technology is seen overtime to modify, control the distribution of drug in tissues, cells, and specific target sites within the body.

5.1 Nanoparticles

One of the technologies used to target drugs to site of interest is the use of nanoparticles that are polymer based. This has been ongoing since 1980s when new discoveries in polymer chemistry led to the design of biodegradable and biocompatible materials [58]. Recently, research focus has been on designing drug delivery systems with sizes between the range of nanometers which are otherwise known as nanoparticles [9, 181]. Nanoparticles are submicron colloidal system that comprises of polymers and they are usually less than 1 μm. That is, they are between 7 and 70 times smaller in size than red blood cells. Generally, nanoparticles loaded with drugs are able to interact with biomolecules within and outside the cell without leading to any irreversible damage. This is because the diameter of the cells in the human body is between 10 and 20 microns while different structural units of cells are between a few several hundred nanometers [89]. Biopolymer-based nanoparticles can be prepared either as nano-spheres or nanocapsules. In nanosphere formulation, drugs are dispersed throughout the entire particle within the polymer while nanocapsules are formed by a liquid core containing drug and surrounded by a polymeric membrane [58]. The use of proteins to prepare nanoparticles helps to obtain the precise size of the desired nanoparticles because their secondary structure determines their molecular sizes. Collagen among other proteins is good examples of proteins that have been designed and utilized as nanoparticles for therapeutic application [144, 165]. Collagen nanoparticle is prepared with additional chemical treatments in order to enhance the mechanical strength [121]. A sustained drug release was displayed by collagen nanoparticle in a recent study. This was attributed to the ease of controlling the particle size, a large surface area, high adsorption capacity, and dispersion ability in water [144]. Furthermore, properties such as large surface area small size, great absorptive capability, capacity to diffuse in water to form a colloidal solution has made collagen-based readily used in sustained and delayed release formulation for steroids and antibiotics. Some of the useful benefits generally offered by nanoparticles are:

- Improved drug solubility and compatibility
- Ability to target tissues and organs that are pathogenic
- Sensitivity to stimuli from external environment (e.g., heating effect of magnetic field or the pathogen stimuli environment (e.g., changes in temperature or pH)
- Ability to transfer a metabolic information reporter. That is, a reporter that supplies information on metabolism [181, 197–199].

The most widely employed methods for fabricating protein-based nanoparticles are emulsification, desolvation, coacervation, spray drying. Other methods include jet-milling technique, fluidization, and solvent precipitation method, and interfa-

cial polymerization. Apart from proteins, polysaccharides have also been used for the manufacture of nanoparticles. They are classified by their native charges, for example, cationic (chitosan), anionic (alginate, heparin, hyaluronic acid), and non-ionic (pullulan, dextran). They can also be classified based on the mechanism of their formation, viz. chemically crosslinked nanoparticles, physically crosslinked nanoparticles, polyion complex, and self-assembled nanoparticles [126]. Chitosan remains the most commonly used polysaccharide for fabricating nanoparticles [163]. Nanoparticles are expected to be excreted from the body after they have delivered the incorporated therapeutic agents. Also, they should be without the risk of uncontrolled accumulation, non-toxic and should not cause any immune response [203].

5.2 Tablets/Pellets

Over the years, polymers have been used as excipients in traditional oral drug release, and they have also been employed to protect drugs from degradation during storage [58]. Pellets are very suitable for local delivery of certain compounds. Bionanopolymers are often used in tablet/pellet formulations as diluents for highly potent low dose drugs. Collagen-based mini-pellets have been synthesized as for the delivery of various compounds. This pellet was used as a carrier for the local delivery of minocycline and lysozyme [56, 113, 122, 192]. Lucas and his coworkers also described a pellet drug delivery vehicle made of purified type I collagen in 1989. This was used as a delivery device for water-soluble osteogenic proteins [111]. Collagen pellets are commonly found in use extensively in Japan, and they are referred to as monolithic devices. They are usually tiny, cylindrical structures (rod-like in shape) with a diameter of about 1 mm and length of 15 mm. They are administered through injection with the aid of a syringe and a plugar [167]. Polysaccharides such as starch and cellulose are used in tablet formation to prevent drug disintegration. These bionanopolymers swell upon hydration, leading to a burst of the tablet. This results in the increased surface area of the drug that is exposed and improved the dissolution characteristics of the formulation [108].

5.3 Gel

Gel happens to be another form in which bionanopolymers are used as drug delivery systems. These gels which can be of protein, polysaccharide, or polyester origin possess unique properties such as the ability to soak and swell when in contact with liquid (biological fluids). They are also able to maintain their integrity after hydration. In addition, they have high bio-adhesion property, easy to apply, and they are compatible with a wide variety of drugs and therapeutic agents [167]. A very common bionanopolymer fabricated in this form is collagen via crosslinking with the chemical. However, they are still capable of forming hydrogels without the

use of chemical crosslinking [178]. The non-fibrillar viscous solution in aqueous medium and fibers injectables suspensions are the most common forms by which collagen is used as an injectable hydrogel. Drugs to be administered are mixed in these suspensions and injected into the body. Initially, it remains as a liquid but after a while, it becomes gel-like and has the potential for controlled and sustained drug delivery [167]. Hydrogels produced by crosslinking chitosan have also been investigated by Wu and his colleagues. They are known to be pH sensitive and have the ability to promote a sustained release of therapeutic agents upon nasal administration [215].

5.4 Capsules

Capsules are alternatives used for tablets and materials that are poorly compressible. They mask the bitterness of some drugs and at times increase the bioavailability of drugs. Over the years, bionanopolymers have been used to "bulk out" capsule fills. Polysaccharides have been exclusively used as a shell material for hard (two-piece) and soft (one-piece) capsules [58]. Capsules that are chitosan-based have also been synthesized for delivery of drugs. This is observed in the novel thermoresponsive ELR/chitosan microcapsules that were developed for the delivery of active molecule [37]. Chitosan-based capsules remedy electrostatic complexation that occurs in most delivery systems. Also, they respond to other external stimuli apart from pH [38].

6 Application of Bionanopolymer in Drug Delivery

The use of bionanopolyers as drug delivery system has been ongoing ever since the discovery of their unique properties. A lot of in vitro and in vivo studies have been undertaken to understand more clearly the mechanism of delivering several therapeutic agents using bionanopolymers. Some of the results obtained have formed the basis for their clinical applications. Protein-based pellets have been proven to be effective and successful for the in vivo delivery of interleukin-2. It was discovered that the half-life of interleukin-2 was prolonged with the use of pellets (half-life 360 min) compared to subcutaneous and intravenous injections of an aqueous preparation (15 and 8 min respectively). It was also proven that a prolonged retention of interleukin-2 was experienced when these mini-pellets were injected subcutaneously [167]. Collagen-based nanoparticles have shown their potential as sustained release formulations for steroids and antimicrobial agents because of their small size, a large surface area, high adsorptive capacity, and ability to disperse in water to form a clear colloidal solution [48]. Rossler and co-workers likewise, observed an enhanced dermal delivery of retinol using collagen nanoparticles as the drug carrier. They reported that the collagen facilitated a quicker and higher transportation of retinol through the skin than the freshly precipitated drug and the drug was stable in the system [164]. There has been an extensive study of collagen-based pellet as a gene delivery vehicle.

One such study is the investigation of the effect of collagen-based mini-pellet on the mRNA expression and functional status of the facial nerve. This experiment was however carried on rat model [92].

Delivery systems that are chitosan-based have been reported for oral, parenteral, ocular, nasal, and transdermal delivery; this is particularly attributed to their mucoadhesive property. Chitosan-based gene delivery system to oral and nasal route gene therapy has successfully been applied. Nanoparticles made from chitosan have also been employed as delivery carriers for growth factors (e.g., epidermal growth factor and fibroblast growth factor) which can be impregnated into a construct for application in tissue engineering [158, 168]. In another study, a chitosan-based biopolymer was used to deliver a hydrophobic drug (ketoprofen). The results from the in vitro release revealed that the bionanopolymer has a good potential for hydrophobic drugs in a pH-sensitive controlled release [155, 156]. In addition, it was observed in another study that grafting acetylated chitosan with a fatty acid such as palmitoyl led to the development of chitosan-based excipients capable of entrapping and releasing drugs that are hydrophobic [79, 101, 120]. Wijekoon and his colleagues also developed a chitosan-based hydrogel that was used to deliver oxygen for wound healing [213]. The hydrogel was synthesized by photo-crosslinking; this hydrogel allowed for the control of both the capacity and rate of the oxygen delivery. It was also able to maintain the level of oxygen for up to five days. Other studies have shown that chitosan has the ability to improve and prolong the absorption of hydrophilic drugs that are ingested orally [213] and via pulmonary administration [8]. Reduced toxicity and enhanced intestinal absorption capability was also demonstrated by chitosan-based nanocapsules for the oral delivery of peptides as reported by Prego and his fellow workers [157]. Similarly, this approach can be applied for the delivery of other drugs like insulin as shown by other studies [80, 116, 117, 224]. Bhattarai and coworkers developed a chitosan-based hydrogel for the controlled release of albumin [18]. The observation from the in vitro release studies is that there was a high release in the first 5 h and subsequently a sustained release over the next days of up to 80% cumulative release. Advantages associated with the use of bionanopolymers as drug carriers have also been reported by some scientist. Nanoparticles of bionanopolymer origin can be absorbed by the reticuloendothelial system [121]. It can also enhance the uptake of exogenous compounds (e.g., anti-HIV drugs) into a number of cells like macrophages [14]. Reports on the use of such nanoparticles as carriers for cytotoxic agents and other therapeutic materials such as camptothecin and hydrocortisone have been made by Yang and his coworkers as well as Berthold and his coworkers respectively [16, 219]. Other advantages that make bionanopolymer widely employed in drug delivery application is the ease of nasal and parenteral administration [191]. This was demonstrated by Wu and his coworkers in an experiment where hydrogels synthesized from bionanopolymers. The hydrogels were used as smart devices for the controlled release of drugs via nasal administration as drops/spray. This study carried out on rat models showed an increased absorption of the therapeutic agent in the nasal cavities, decreased level in the blood, and no sign of cytotoxicity. These results demonstrated that bionanopolymeric hydrogels have potentials as drug carriers for controlled release of therapeutic agents, especially molecules that are hydrophilic in

nature [216]. Currently, several in vivo and in vivo studies are still going in order to discover other possible applications of bionanopolymers for the successful delivery of different therapeutic agents used in the treatment and management of several diseases.

PHAs like other degradable biopolymers have gained grounds in the application as a drug delivery vehicle for the administering several drugs since the early 1990s. When converted into films, matrices, microcapsules, microsphere and nanoparticles, drugs can be entrapped into this formulation for different drug delivery application. Microcapsules made of PHAs have been widely used for the delivery of drugs such as anesthetics, antibiotics, anti-inflammatory agents, anticancer agents, hormones, steroids, and vaccines [139, 142]. The potential application of some PHAs such as P(3HB) and P(3HB-*co*-3HV) have been investigated in a number of in vitro and in vivo studies for drug delivery purposes. Gangrade and price reported the use of PHA microsphere as vehicles for steroids [59]. In their investigation, PHB and P(3HB-3HV) were used to synthesize microspheres entrapped with progesterone and the in vitro release was carefully studied. Also, PHB, PHBV, and P(3HB-4HB) showed to be advantageous in the design of biodegradable, implantable rods for delivering antibiotics in the treatment of chronic osteomyelitis [66, 200, 218]. PHAs are known to have the ability to provide and maintain adequate concentrations of antibiotics at sites of infections [63, 67]. In addition, the in vivo and in vitro releases of anticancer agent (lomustine) from PHA and a synthetic polymer were compared, and it was discovered that the drug release kinetics from the PHA microsphere was better [22]. In another study done by Sendhil and coworkers, microspheres and microcapsules of polyhydroxybutyrate-*co*-hydroxyvalerates (PHBV) of various 3-hydroxyvalerate contents were loaded with tetracycline. The drug carrier (PHBV) was subsequently used for the targeted treatment of some periodontal disease, and it was observed that the release of the drug was complete before any sign of degradation of the carrier [172]. Similarly, PHB (polyhydroxybutyrate) microsphere was used to deliver an antitumor drug (rubomycin) to mice, and it was observed that the proliferation of the cancer cells was greatly inhibited compared to the free drug [179]. In the same vein, Kawaguchi and colleagues synthesized PHB-based microsphere for the delivery of 2, 3-diacyl-5-fluoro-2-deoxyuridine in mice and rats. Results showed low toxicity, good compatibility, and excellent drug efficiency [85]. In a recent study by Lu et al., a sustained release of P13K inhibitor (TGX221) was achieved using PHA nanoparticles and the proliferation of cancer cell lines was successfully hindered [110]. Furthermore, the efficacy and bioavailability of cisplatin embedded in a novel amorphous amphiphilic block copolymer P(3HV-*co*-4HB)-*b*-mPEG was studied by Shah and fellow researchers [174]. Reports from their observation showed that there was a sustained release of the drug from the drug carrier as well as tumor growth suppression by the nanoparticles. It was concluded that the PHA-based nanoparticle had an enhanced apoptotic effect on the tumor cells. These and other reports from several scientists globally have proven that bionanopolymers are potential drug delivery systems for a wide range of therapeutic agents.

7 Challenges

Despite the fact that, bionanopolymers have great properties that make them widely employed in biomedicine as drug delivery devices. They have somewhat been limited in use because they have not been able to successfully and completely deliver certain classes of drugs. Thus, there is still a big gap that needs to be bridged in order for major needs in drug delivery systems to be met. Also, at the moment, there is a need for a lot of improvements and modifications to be made on these bionanopolymers before they can be largely applied clinically. Furthermore, another challenge is the feasibility of scaling up the production of this bionanopolymer in the market. Also, the possibility of designing multifunctional drug delivery systems that can meet the different biological and therapeutic need still pose to be a challenge with the use of these bionaopolymers.

8 Conclusion

There has been increased interest in the use of bionanopolymers for medical application in response to the need to efficiently manage several diseases. This has led to considerable advances in drug delivery technology. Bionanopolymers have various advantages over most synthetic polymers in several biomedical applications. Hence, the main reason behind its application in the area of drug delivery. The use of bionanopolymer as drug carrier is majorly attributed to their biodegradability, versatility, and broad range of properties. Various successful studies using bionanopolymers have proven that they are biocompatible for drug carrier use. They can be formulated for targeted drug delivery in a controlled manner. Thus, bionanopolymer-based drug delivery vehicles hold tremendous promise in the management of several disease conditions such as cancer. With the intense research ongoing in this area, bionanopolymers will emerge as one of the most economical and environmentally friendly material for the next generation in a wide range of biomedical application. Their synergism with other bioactive compounds will greatly contribute to further development and advancement of drug delivery technology. This will also bring many bionanopolymer-based products to the market.

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Chapter 9
Polylactic Acid-Based Nanocomposites: An Important Class of Biodegradable Composites

M. Ameer Ali and A. Shanavas

1 Introduction

The majority of polymers, especially plastics, are synthesized from the distillation and polymerization of non-renewable petrochemical-based monomers like olefins including ethylene, propylene, styrene and vinyl chloride, etc. They are non-degradable, and the disposal of them poses a serious environmental problem. Hence, the society needs a bio-based, environmental-friendly and non-toxic bio-compatible polymers for sustainable resources [2, 3, 23].

Natural macromolecules such as proteins, cellulose and starch are generally degraded in biological systems through hydrolysis followed by oxidation [19]. Hence, most of the reported synthetic polymers (based on amine, enamine, ester and urea) are found to be having hydrolysable backbone which could susceptible to biodegradation by microorganisms and hydrolytic enzymes. Among the common synthetic biopolymers with good degradability, polylactic acid, polyacrylamide, polyethylene glycol, etc. are important.

The biodegradation of polymeric material is a complex process that can proceed through either by depolymerization of the macromolecules into shorter chains or mineralization by enzymes [20, 33]. In this process, a small size of oligomeric fragments is formed which will be transported into cells where they are bio-assimilated by the microorganisms and then mineralized.

Degradation property of polymers depends on the nature of the site, microstructure, branching in molecular chain, hydrogen bonds, solubility, diffusion, etc. [41]. Regularity in polymer chains enhances the crystallization which making the

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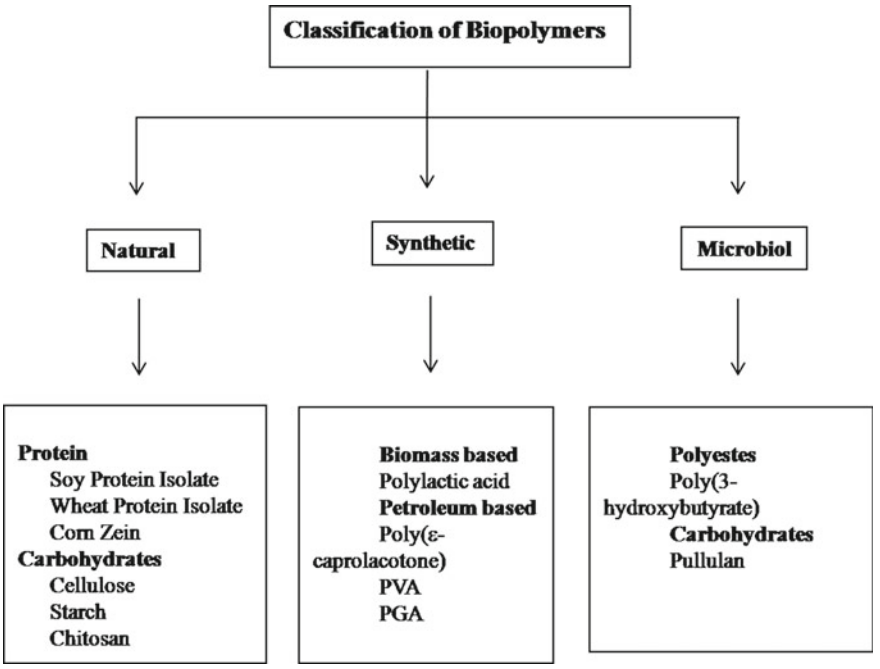
hydrolysable groups inaccessible to enzymes whereas the amorphous-crystalline polymers enhance biodegradability due to the size and shape [41]. Also, both radiation and chemical exposure on polymer speed up the rate of biodegradation. Moreover, polymers with high molecular weights are generally immune to biodegradation. For example, polymers such as polyethylene (PE), polypropylene and polystyrene hinder the microbial growth because of its high molecular weight [41].

The commercial products available in the market like packaging materials (trash bags, wrappings, loose-fill foam, food containers, film wrapping, laminated paper), disposable non-woven (engineered fabrics) and hygiene products (diaper back sheets, cotton swabs), versatile medical products including sutures, bone screws, carriers for controlled drug release, consumer goods (fast-food tableware, containers, egg cartons, razor handles, toys) and agricultural tools (mulch films, planters) are being the backbone of the development of biopolymers (Armentano et al. 2013; [8, 38]).

A recent market survey shows that PLA is one of the most preferred biopolymer. PLA has several advantages by comparing with other petrochemical-based polymers due to the factors like lower gas emission, lower energy consumption and no toxin release during biodegradable process [1]. The US Food and Drug Administration (FDA) approved that PLA is biologically safe [1].

1.1 Classification of Biopolymers

Biodegradable polymers can be classified as natural and synthetic biodegradable polymers [13]. The natural biodegradable polymers are originating from natural resources such as starch, cellulose, chitin, chitosan, lignin and proteins [29]. The synthetic biodegradable polymers are synthesized from bio-derived resources like corn and starch [13]. Besides, another class of biodegradable polyesters also produced using microorganisms [13]. These polymers such as poly(hydroxyalkanoate)s, including poly(-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), are synthesized using enzymes. The synthetic aliphatic polyesters such as polylactic acid (PLA), poly(-caprolactone) (PCL), poly(butylenes-succinate) (PBS) and poly(ethylene-succinate) are synthesized using the common methods like direct polymerization and ring-opening polymerization.



2 Polylactic Acid (PLA)

Polylactic acid (PLA) is aliphatic polyester which is synthesized from bio-derived or natural resources such as corn starch, cassava roots, chips or starch or sugarcane [22, 29]. Since PLA is derived from renewable and biodegradable resources, its degradation products are non-pollutant and non-toxic [45]. Hence, PLA is a suitable green alternative for the petrochemical commodity plastics which are commonly used in packaging of foods, agricultural products, disposable materials, textiles, etc. [24]. Additionally, PLA has several bio-applications also like surgical implants, sutures and drug delivery systems [12, 31, 40]. PLA is an immunologically inert synthetic polymer. Hence, it is used for designing a composition of tissue engineering scaffold [26].

Generally, there are three kinds of PLA such as poly(D-lactic acid) (PDLA) derived from D-lactic acid, poly(L-lactic acid) (PLLA) derived from L-lactic acid and D,L-PLA (PDLLA) derived from racemic mixture of lactic acids. Scheme 1 illustrates the structure of L-, D- and DL-lactic acids [11, 57]. The preparation of polylactic acid is achieved through various methods/approaches including in situ polymerization, solution method, melt blending and melt intercalation [39, 44].

D-lactic acid L-lactic acid DL-lactic acid

Scheme 1 Structure of L-, D- and DL-lactic acid

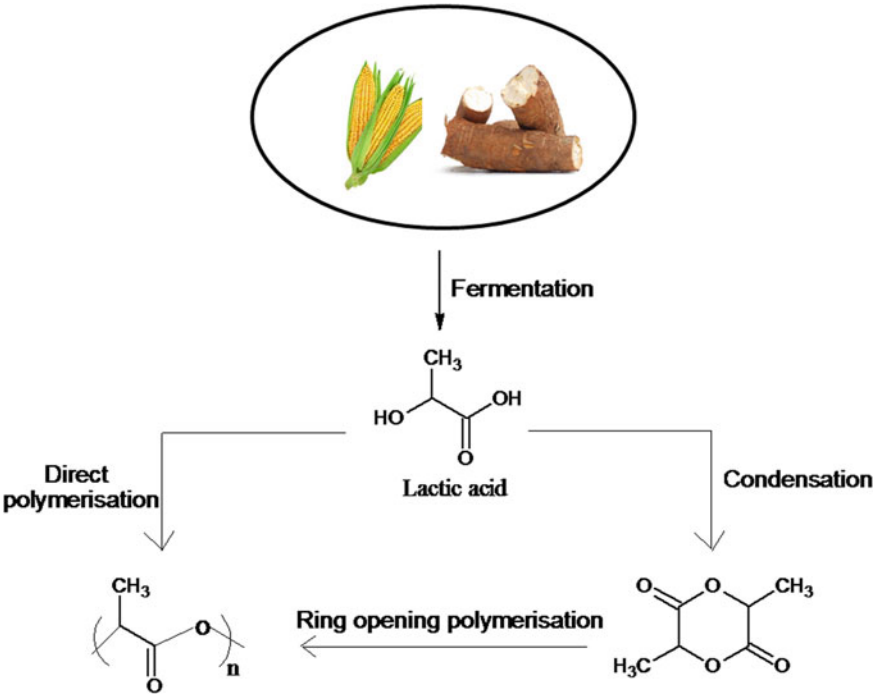
Table 1 Physical properties of PLA

Molecular weight (Mw)	100–300
Glass transition temperature (Tg)	55–70 °C
Melting temperature (Tm)	130–215
Degree of crystallinity	10–40
Tensile modulus, E	1.9–4.1
Decomposition temperature	500–600 °C
Young's modulus	3600 MPa
Elongation at break (%)	100–180
Density	1.25 kg/m^3
Degradation time	50% in 1–2 years

2.1 Properties of Polylactic Acid (PLA)

The properties of polylactic acid (PLA) are determined by many factors such as the temperature, viscosity and molecular weight. Table 1 lists the physical properties of PLA. It has a high elastic modulus, tensile strength and it is quite brittle. It is a carbon-neutral bio-plastic; thus, it can be synthesized from renewable resources. PLA is primarily hydrophobic; however, it is more hydrophilic than polyester (PET). Further, PLA is stable up to about 500 °C and its thermal decomposition occurs in single stage at 500–600 °C range.

Polylactic acid has reasonably good optical, physical, mechanical and barrier properties compared to existing oil-based polymers [32]. However, some of the physical properties of PLA are often not good enough to meet the global demands. Hence, some of the potential applications require a high level of mechanical, thermal and flame retardant properties. This problem can be overcome by incorporating the various nanofillers into the PLA matrix. Incorporation of nanofillers such as carbon nanotubes, graphene, TiO_2, ZnO, layered silicates (montmorillonite (MMT), hectorite, and saponite), graphene, fullerene and metal oxides enhances the biodegradation rate, mechanical strength, crystallinity, bio-adherence, hydrophilicity, morphological properties, thermal and photochemical degradation [5]. Homogeneous and fine dispersion of nanoparticles into polymer matrix makes a strong interfacial adhesion between the phases of polymers and nanofillers.



Scheme 2 Life cycle of PLA

3 Life Cycle of PLA

Scheme 2 illustrates a life cycle of PLA, which starts from bio-derived natural resources that will undergo the fermentation process and gives the lactic acid. The conversion of lactic acid to polylactic acid is achieved by the direct condensation of lactic acid or ring-opening polymerization (ROP) through the formation of cyclic dimer intermediate. The former method involves solvent and high vacuum whereas the later one is a solvent-free method [18]. The metal-catalyzed ring-opening polymerization reaction of cyclic dimer intermediate yields the polylactic acid. The complex of metals such as Mg, Zn, Sn, Fe, Sm, Lu, Ti and Zr are used as catalyst. Among these complexes, Stannous bis-2-ethylhexanoate [$Sn(Oct)_2$], highly soluble in organic solvent, is the most preferred and standard catalyst for the ring-opening polymerization. This catalyst is patented by Cargill (USA) in 1992 [15, 17, 30].

4 Importance of Nucleating Agents

Nucleation is the process of crystal formation from a solution, a liquid or a vapor in which ions, atoms or molecules arranged in a pattern, a characteristic of crystalline of the material. Consuming longer time for the crystallization of PLA is one of the major problems in the large-scale production of PLA. Several methods adopted to make a fast crystallization as to increase the nucleation. The addition of nanofillers or heterogeneous nucleating agents is one of the methods to speed up the crystallization rate. The crystallization kinetics of PLLA could be accelerated by the nanofillers of both graphene and CNTs which act as nucleating agents. As compared to graphene, the ability to accelerate the crystallization induced by CNT is much stronger. Amorphous nanosilica is also used as nucleating agent in thermoplastics [9, 14, 54].

5 Effect of Plasticizer on PLA

The physical properties such as mechanical and thermal stability of PLA can be enhanced through the incorporation of plasticizers. The addition of plasticizers like acetyl tri-n-butyl citrate (ATBC) and poly-(ethyleneglycol) (PEG) favorably changes the mechanical properties of PLA. Besides, an analysis of the glass transition temperatures of the different plasticized PLA shows abrupt changes in elongation while Tg is lowered to 35 °C. Further decrease in temperature, changes the mechanical behavior of plasticized PLA from fragile to ductile [6].

The thermal stability is also an important factor to determine the processing feasibility of biodegradable polymers in industry. Thermal stability of the PLA nanocomposites depends significantly on the thermal stability of the organic modifiers [34]. For example, 1,2-cyclohexanedicarboxylic acid diisononyl ester (Hexamoll®DINCH) is a plasticizer for the manufacture of flexible plastic articles in sensitive applications like toys, medical devices and food packaging [16]. However, the incorporation of organic montmorillonite into DINCH plasticized PLA can improve the compatibility of nanocomposites [52, 53].

6 Polylactic Acid-Carbon Nanotube (PLA/CNT) Nanocomposites

Due to the high tensile strength, stiffness, better electrical and magnetic properties, carbon nanotubes (CNTs) are considered as the important nanofiller material for the preparation of polymer nanocomposites [34]. Especially, CNT is suitable for the preparation of polymer bio-nanocomposites because its incorporation into polymer matrix improves the solubility, degradability, biocompatibility and other needed physical properties [36]. It is expected that the continuous research efforts

on the structure-property relationships of pure CNT and functionalized CNT in the interdisciplinary areas like toxicological and pharmacological fields will make the society to enjoy the safe products of them in biomedical applications. The incorporation of CNT into PLA matrix results in the promising functional biomaterials having potential biomedical applications. For instance, the investigation of Supronowicz et al. reveals when the alternating current was applied onto the PLA/MWCNT composites, the osteoblast proliferation and calcium production improved significantly [50].

There are a number of papers have been published in which how the different properties of PLA/CNT nanocomposites vary with varying parameters have been explained [21, 36, 50, 56]. For instance, Wu et al. reported that the role of aspect ratio of CNTs on modulus of PLA/CNT nanocomposites [55]. While the PLA nanocomposites with high aspect ratio CNT have high modulus, the study on same with low aspect ratio CNT exhibits low modulus. The work of Moon et al. indicated that the loading of CNT into the PLA matrix decreases the tensile strength and ultimate elongation whereas increases Young's modulus of the material [37]. Further, the authors added that the loading of CNT increases the thermal stability and decreases the electrical surface resistivity. It is evident from the works of many researchers that the incorporation of MWCNT into PLA improves the thermal stability and mechanical properties significantly [34, 36, 50]. Wu et al. investigated on crystallization and biodegradation behavior of PLA/CNT nanocomposites and found that the addition of CNT improves the crystallization rate. Further, the crystals formed with defect structure degraded comparatively faster than those with regular crystalline structure.

7 PLA/Layered Silicate Nanocomposites

Inorganic nanoparticles are used as additives to enhance the polymer's performance [42]. Layered silicates are most commonly used for the preparation of polymer-layered silicate (PLS) nanocomposites. These layered silicates are montmorillonite (MMT), hectorite and saponite [45, 46]. However, the incorporation of the montmorillonite clay into PLA decreases the toughness of the PLA-nanosilicate composites [27, 28, 35, 43]. This could overcome by the addition of polyethylene glycol (PEG) which acts as a good plasticizer into PLA/clay systems [48, 51]. Also, MMT/PLA matrix did not affect any changes in glass transition temperature (Tg) and melting temperature (Tm) of PLA nanocomposites. In addition to that the incorporation of nanoclays into a polymeric matrix can also enhance its thermal stability. This is mainly due to the dispersed silicate layers that hinder the diffusion of volatile decomposition products out of the materials, delaying the release of thermal degradation products in comparison with the pure polymer. Further, the thermodynamic quantities such as entropy and enthalpy factors determine the morphological arrangement of the clay nanoparticles in the polymer matrix.

8 PLA/Metal and Metal Oxide Nanocomposites

TiO_2 is a non-toxic, inert and inexpensive material which is widely used in paints, cosmetics, food packaging materials as well as photocatalyst in waste water treatment [10]. It has a strong adhesive force. The adhesion between hydroxyapatite [$Ca_5(PO_4)_3(OH)$], and PLA is very poor. It can be enhanced by the addition of TiO_2 nanofiller which makes a uniform dispersion and strong interfacial interaction between HA and PLA layers. The uniform dispersion of TiO_2 into PLA matrix changes the optical properties of pure PLA. For instance, the transmittance of pure PLA ($T = 87\%$) is reduced significantly by the addition of TiO_2 nanoparticles [10].

ZnO is a well-known environmentally friendly and multifunctional inorganic filler which have a strong UV-light screening effect [7]. This causes a drastic photodegradation of polymer nanocomposites. Also, the rate of degradation of the PLA and ZnO nanocomposites strongly depends on ZnO content [7]. The interface between the ZnO nanoparticles and the PLA matrix plays a key role in the structure-property relationship. The literature search reveals that the incorporation of ZnO into PLA matrix increases the mechanical properties such as tensile strength, Young's modulus and decreases the nominal strain at break [7].

The incorporation of Ag into PLA matrix reduces Young's modulus from 2900 to 2100 MPa, elongation at break from 0.036 to 0.031 mm/mm and ultimate tensile strength from 55 to 45 MPa. Maria and Sylwia found that the introduction of nanosilver to PLA matrix reduces the photodegradation of PLA which may be due to the possible photo-redox reaction between Ag and PLA or the degradation products of PLA [47]. In contrast, they observed the thermal degradation of PLA is accelerated by added nanosilver [47].

9 Application of PLA

PLA-based nanocomposites find its applications mainly in the area of packaging materials, materials for automobiles, materials for biomedical applications, etc. The biomedical applications include reconstruction of damaged tissue, artificial supports for cell growth, drug delivery products, protein encapsulation, ligating clips, bone pins, rods, anastomosis clip, angioplastic plug, suture anchor, etc. [12, 31, 40]. The packaging materials such as flexible packaging films, cold drink cups, cutlery, apparel and staple fibers, bottles, injection and extrusion molds, coatings, toys, lined paper cups (Fig. 1), aprons, coffee cup, tea bags and thermoformed packaging are the very common products from PLA, which are consumed by the people throughout the world [4, 49]. The products such as injection molded parts, door panels, door handles, instrument panels dashboards, seat cushions, cabin linings, fuel systems, engine covers, timing belt covers and bumpers are from PLA nanocomposites used in automobile industries [25].

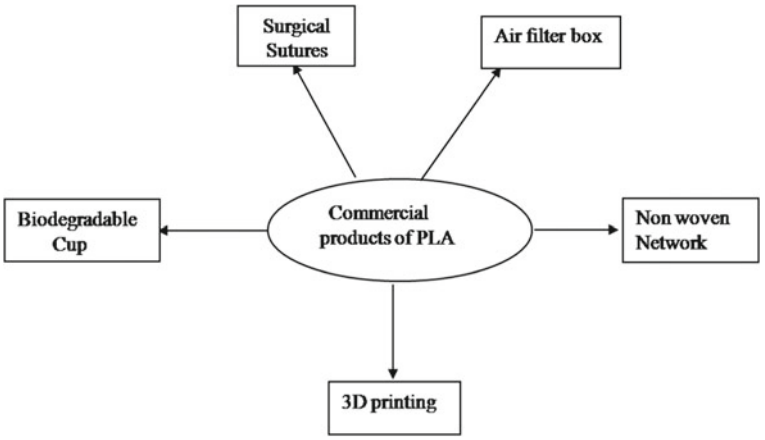


Fig. 1 Commercial products of PLA nanocomposites

10 Conclusions

In last two decades, a huge amount of research efforts have been put forth from the different parts of world to develop the research of PLA-based nanocomposites from basic to application-oriented status. This not only contributed to the improvement of knowledge and a better understanding of subject but also it ends up with many fruitful commercialized products which are now being the essentials for day-to-day life. Although the techniques related to the uniform dispersion of nanofillers, its controlled release during the synthesis of PLA nanocomposites and to improve the rate of biodegradability are still in progress.

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Chapter 10
Biopolymers in Medicine

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1 Introduction

Biomaterials are materials that are made to serve as a possible replacement for tissues, organs or body systems. They are made in such a way that they are able to support the body system in whole or in part. They may also augment the body part or system such that they play a supportive role in the system. Biological systems include respiratory, nervous, digestive, circulatory, reproductive, muscular, endocrine and integumentary systems. These systems have several organs that work together as a unit in order to keep the body functioning. At some point, the body tissue or organ may be weak, overworked or completely damaged and may lead to either replacement, augmentation or complete removal. In achieving the functions of the biological system, wherein a case there is a need for complete replacement; artificial materials may be produced to serve the same purpose in place of the biological organ or tissue. This led to the production of biomaterials several years back. Materials such as plant leaves, fruits, stems and roots, linen, silk, flax, hair, grass, animal gut, natural dyes, hides and skin were used in wound healing, disease/infection cure, skin cure and skin care by the ancient Egyptians and Indians. Materials that gradually

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become integrated into the biological system with time are now given preference over materials that remain steady in the body due to the fact the pros associated with such materials far outweigh the cons associated with them. Whereas the former are regarded as bioresorbable biological materials, the latter are referred to as stable biological materials. Such bioresorbable materials could be used to replace skin and soft tissues, bones and cartilages, organs and muscular tissues.

Bioresorbable materials are given consideration over bio-stable materials in biomedical applications because of their ability to coexist biologically with implants already in biological systems, their ability to be assimilated into the body and the favourable position of not expelling or replacing them when they are never again required or are corroded, in this manner keeping away from rehashed surgeries. There are likewise developing novel biomedical innovations, for example, tissue engineering, regenerative medicine, gene therapy, controlled drug delivery and bio-nanotechnology, all of which have to do with the utilization of bioresorbable materials [11]. With the current trend, a forecast would show that bioresorbable devices that could help in the fixing and recovery of impaired tissues, biological implants, artificial limbs and artificial organs might supplant huge numbers of the changeless prosthetic devices.

2 Definition of Terms

2.1 Tissue Engineering

Tissue engineering is a field of study that aims at creating medical devices that, once introduced into the body, will act as a replacement or rather an enhancement of tissue function, which has been weakened by maladies by bacteria/virus, damage or age. Tissue engineering involves the use of tissue scaffolds, to form new tissues for medical purposes.

2.2 Regenerative Medicine

Regenerative medicine is used alongside tissue engineering in treating wounds, injuries, skin diseases and infections, using specially grown tissues, cells and artificial organs, to speed up the natural healing processes or assume the role of a completely damaged organ.

2.3 Gene Therapy

Gene therapy is the transplantation of the usual gene into cells to substitute the defective or missing gene in order to correct genetic disorders.

2.4 Controlled Drug Delivery

Controlled drug delivery is a system used in medicine that delivers healing agents in the form of drugs to the target site in the body, and maintains the desired concentration for enough time, without causing harm to the affected site.

2.5 Bio-Nanotechnology

Bio-nanotechnology is the science of finding ways of applying nanotechnology in biological systems. Skin regeneration is amongst the areas of application, which can be led in-vitro, allowing the chance to mostly build up the host tissue additional physically, trailed by implantation. A perfect scaffold must display a permeable, interconnected and porous structure to allow infiltration of cells and supplements. It ought to, likewise, show the suitable surface structure and science for cell adhesion and multiplication. The perfect scaffold should be characterized by physical and morphological qualities very close to, if not better than those of engineered tissues for biomedical applications. It should be prone to biodegradation in a way that it breaks down to form dissolvable non-harmful products when the tissue is completely created within the body.

2.6 Resorbable Biomaterials

Resorbable biomaterials undergo bio-resorption, a case where the polymer or biomaterial undergoes degradation into products that are produced by simple hydrolysis and is expelled from the body by cell action. Resorbable biomaterials are materials that degrade safely into or within the body over a period of time.

2.6.1 Requisites for Resorbable Biomaterials

First and foremost, in other for a material to be certified as a resorbable biomaterial, it should be biocompatible with the body. That is, the biomaterial's ability to receive and respond to apposite host in a specific application. Secondly, a resorbable biomaterial

should show that it can stay within the biological fluid systems over a long time without initiating impairment to host body by way of infection, discomfort or pain due to corrosion, malfunction or disruption of biological activities in the body. It should be noted that with time, there could be property changes in terms of chemical, physical or biological properties of the resorbable biomaterial caused by degradation [6]. In recent times, polymeric biomaterials have been synthesized to be resorbable.

2.6.2 Biocompatibility

Generally, for a polymeric material to be resorbable, it should be non-toxic, non-inflammatory, non-immunogenic and non-carcinogenic. By this, the material would not cause any medical harm to the body when applied.

2.6.3 Biofunctionality

For biofunctionality of biomaterials, it is necessary that the biomaterial should;

- Have adequate mechanical properties over time
- Safely remove degradation products
- Be stable during sterilization
- Last long during service
- Have good permeability
- Be easily processed for the intended application
- Exhibit good degradation rate.

3 Fibre-Forming Polymers in Medicine

Fibre-forming polymers are making inroads in resorbable biomaterials technology. Most medical devices are made of biopolymer and bioresorbable materials in the form of gels, scaffolds and surgical threads. The physical and mechanical requirements of the medical devices required for their end-uses are based on the technological advancements made in the chemistry, synthesis and processing of synthetic fibres and textile technology. Fibre-forming polymers are synthesized to have high molecular weight, linear structures without bulky groups and side groups in their main chain. For the fibre-forming polymers, crystallization during stretching is greatly enhanced by the linearity of the main chains that allow intermolecular attractive forces to effectively bind the chains together [5]. They are designed and applied in medicine and medical devices as ‘bio-textiles’, for application in the biological environment for the inhibition, diagnosis or treatment of skin inflammations, cuts, wound or diseases and whose execution in enhancing well-being and health of the patient relies on their biocompatibility and bio-stability with cells and organic fluids. However, ‘novel bio-

textiles' have progressed to use the ability of numerous non-woven, woven, knitted, braided and auxetic textile assemblies in medicine and surgery. When such textiles fabricated with fibre-forming polymers are able to degrade and re-integrate into the body system without causing harm to the body, they are termed bioresorbable textiles. Textile structures consisting of bioresorbable fibres offer certain unique properties as medical devices. For instance, a braided dimensionally stable suture is required to give the needed strength and flexibility to grasp edges of a skin cut or wound together for it to heal. In addition, a tissue scaffold made of a bioresorbable textile material would be able to maintain its characteristic form, shape and size while resisting the shear, compressive and tensile forces enforced by circulating body fluids, growing cell bodies and surrounding bones and tissues as the case may be, without inflicting harm to the body. It is therefore, necessary that these factors are considered top priority when synthesizing bioresorbable fibre-forming polymers for tissue engineering and construction.

3.1 Advantages of Fibre-Forming Polymers

There are several advantages associated with fibre-forming polymers. They comprise;

(a) Fibre-forming polymer must be able to withstand the stress of repeated needle penetration by the physician, doctor or surgeon during the patient's surgical operation, treatment or therapy.
(b) Fibre-forming polymer substrates should be resistant to high fatigue.
(c) They should have their dimensions in the nanometre range. In other words, they have a large surface area for cell add-on for unhindered drug delivery.
(d) They should have a structure that makes it possible for the material that will be collapsed or packed little volume for less intrusive delivery through a catheter.
(e) The fibre-forming polymer should be lightweight, thin and flexible.
(f) In addition, they should be tough and should have significant strength on tension.
(g) They should have a porous morphology.
(h) The fibre-forming polymer should have a structure that boosts permeation and multiplication of cells for better tissue construction, restoration and compatibility with biological systems.

3.2 Requisites for Fibre-Forming Polymers

Polymers that undergo a process of forming viscous melt or solution can be spun into filaments or fibres. Low molecular weight sugar solution could be spun into fibres to make 'cotton candy', but ensuing fibres would not have sufficient mechanical properties for bio-textile applications. Therefore, there are preconditions for polymers to qualify as fibre-forming polymers, enabling them to be spun into fibres, staple

and continuous filaments meant for various applications. The preconditions, which are largely based on chemical and structural formula of the molecular chains making up the polymer, also makes it possible for the resulting fibre material to have suitable physical, mechanical and thermal properties. The degree of crystallization, which determines the microstructure, shape, dimensions and orientation of the crystallites, also depends on the chemical and structural formula of the molecular chains. Therefore, not all polymers fall into the category of fibre-forming polymers. A fibre-forming polymer ought to have a synthetic structure which enables it to be spun into filaments that is inclined to forming an oriented crystalline structure on elongation or pulling.

Preconditions for a polymeric material to be fibre-forming are enumerated thus;

(i) The polymer must be of high molecular weight.
(ii) The molecular chains must be linear, with no bulky groups present in the backbone chain.
(iii) The polymer chains must not be prone to cross-linking reactions.
(iv) Intermolecular bonding should be very minimal or totally absent.
(v) There should be no side chains. Such side chains do not encourage close packing of the main chains on cooling.
(vi) The polymer should have the ability to dissolve in a suitable solvent.
(vii) The polymer should be capable of being processed by melt extrusion.
(viii) The polymer should neither have a very low nor a very high melt viscosity so as to enable smooth processing.
(ix) The melting temperature is not close to the decomposition temperature.
(x) In terms of tacticity, fibre-forming polymers should be isotactic with less complex repeat units that make it impossible for molecular chains to crystallize on stretching.

3.3 Fibre-Forming Polymers and Their Manufacturing Processes

3.3.1 Poly (α-Esters)

Poly(α-esters) have been studied extensively having been one of the earliest bioresorbable polymers synthesized and applied by Biomedical Engineers and Technologists. This class of polyesters that have been given tremendous attention by researchers is the poly(α-hydroxy acids), including poly(glycolic acid) (PGA), stereoisomers of poly(lactic acid) (PLA) and their copolymers. They have been researched for structure–property relationship, degradation mechanisms, biocompatibility and wound-healing capabilities [6, 16, 17]. Aliphatic polyesters based on poly(α-esters) are scrutinized as follows.

3.3.2 Poly(Glycolic Acid)

The earliest fibre-forming polymer examined for biomedical applications is poly(glycolic acid) (PGA). Owing to its biodegradability and biocompatibility with the body system, it is a good bioresorbable material. PGA is an extremely crystalline polymer having between 45% and 55% crystallinity. For a similar reason, its dissolvability is restricted to just a couple of solvents. For example, hexafluoro isopropanol ($(CF_3)_2CHOH$) solvent may be used to dissolve PGA. The glass transition temperature (T_g) varies from 36 to 40 °C, and melting point (T_m) ranges from 224 to 230 °C. It is a suitable fibre-forming polymer. Fibres from PGA reveal great strength and modulus. PGA is a bulk-degrading polymer. In the body, polyglycolides are broken down to glycine, which can be defecated in urine or transformed into carbon dioxide and water through the citric acid cycle. Owing to its speedy degradation, PGA is investigated for short-term tissue engineering scaffolds. It is frequently developed into a mesh network and utilized as a scaffold for bone, cartilage, tendon, dental and spinal nerve regeneration.

3.3.3 Poly(Lactic Acid)(PLA)

PLA is given attention because of its relative availability, cost-effectiveness and bioresorbable character. Having been extensively worked on and commercially developed, its general acceptability has been largely hinged on the material's biocompatibility with the body fluid and tissue system, relative high strength and modulus of elasticity, processing ease and obtainability from renewable resources like corn, potatoes, starchy crops and synthetic sources. The material is soluble in various organic solvents. The characteristics already mentioned, have made PLA a material of choice for several biomedical applications.

3.3.4 Poly(lactide-co-glycolide) (PLGA)

PLGA has been a multipurpose biopolymer. Meanwhile, it permits modification of properties, for example, strength, rate of resorption and other applicable biomedical properties, for the purpose of wound healing, by varying the percentage composition of the two major polymers used in synthesizing it; polylactic acid and polyglycolide. Poly (L-Lactide), L-, poly (D-Lactide), D-, and poly (DL-Lactide), DL-lactide, have been utilized in seperate situations for the copolymerization of PLGA. During synthesis, depending on component ratios of glycolide and lactide, the PLGA material may be tailored for a specific purpose [8]. Several PLGA copolymers have been synthesized, explored and developed commercially, for different applications. PLGA copolymers appear amorphous in nature and show glass transition temperature in temperature of between 40 and 60 °C. PLGA may be melted in a wide range of solvents, for *example*, acetone, ethyl acetate, tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), trichloromethane or chloroform ($CHCl_3$), carbon tetrachloride (CCl_4) and

other chlorinated solvents. Because of its tailored mechanical properties, PLGA has been utilized as a suture material over a period of time. In other to obtain high strength, resorbable PLGA for surgical suture material, a higher concentration of glycolide relative to the concentration of lactide, is added during synthesis. This composition induces the quality of a longer strength-retention time, making its complete resorption time between 3 and 4 months. PLGA has been outstanding biomaterial for tissue engineering scaffolds; it reveals worthy cell-bonding and propagation properties. PLGA is applied in other to facilitate tissue regeneration, but unlike its homopolymers, PLGA is degraded by a bulk erosion procedure.

3.3.5 Polydioxanone (PDO)

In order to take care of the weakness in sutures after surgical operations, poly(ester-ethers) which are characterized by thicker and stronger monofilament yarns were developed. This class of polymer-based biomaterials is the polydioxanone (PDO). PDO is a glycolide-derived bioresorbable polymer with poly(ester-ether) linkages, which pass on superior strength and flexibility to the polymer. Integration of the ether segment into the repeat unit lessens the density of ester linkages and decreases intermolecular hydrogen bonds. However, as a result of the reduced number of ester linkages, its degradation rate is reduced.

3.4 Manufacturing Processes

The polymers are synthesized in the form of resin or pellets through various forms of polymerization processes. They are then spun into staple, monofilament or multifilament fibres. The spun fibres are further woven, knitted or braided into fabrics. Non-woven fabrics are not left out from the scheme of production. Thermal, mechanical, chemically bonded or hydro-entangled staple or filament fibres produce non-woven bio-textiles [11]. At the finishing stage and before use as bio-textiles, they are inspected, sterilized and then packaged. The scheme of production of bio-textile end products made from polymer resins is presented in Fig. 1.

4 Non-fibre-Forming Polymers in Medicine

Non-fibre-forming polymers are polymer hydrogels. Hydrogels are unusual forms of polymers that have a vast ability to absorb great volumes of water. They may be natural or artificial. They may be tailored to suit an application in a biological system. They have the capability to modify their chemical structure thereby inducing volume changes due to the physical, chemical and environmental conditions, for example, pH, temperature, salt concentration, electric field and amount of solvent, therefore,

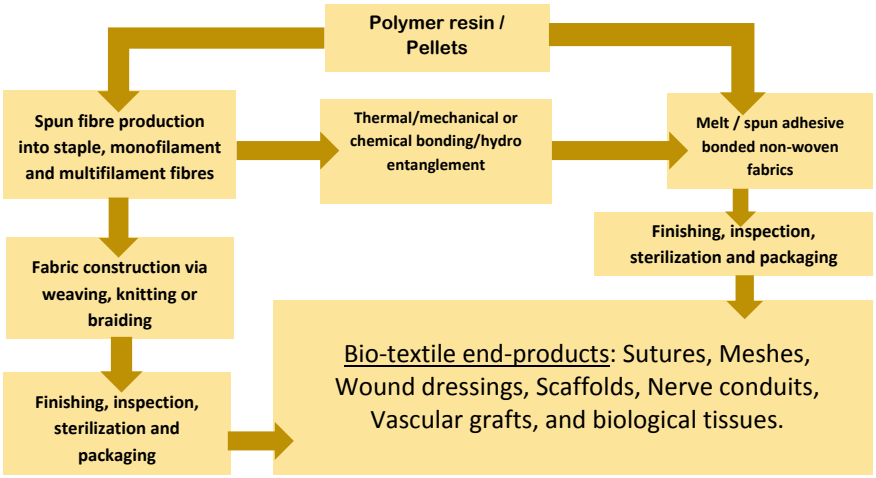

Fig. 1 Bio-textile end products, made from polymer resins: Scheme of production

making the materials stimuli-responsive smart polymers. Best significant property is inflammation behaviour of cross-linked 3D polymer networks. Several researchers have reported that the cross-linking and charge densities of these polymer networks directly affect inflammation and elastic behaviour. Hydrogels display an important non-ideal feature of spatial gel inhomogeneity referring to non-homogeneous cross-linked density distribution that lessens optical clarity, strength, degree of ionization and movable counter ions of hydrogels.

4.1 Polymer Scaffolds in Medicine

Production of scaffolds in medical applications is increasing at a fast speed. Scaffolds perform a crucial role in scaffold-based tissue engineering. Scaffolds should have few significant characteristics. They must be bioactive with target biological systems to the extent of responding to biological environment stimuli. They should have a porous microstructure with appropriate surface chemistry in other to permit cell attachment, proliferation and differentiation. Scaffolds should also have adequate mechanical, chemical and biological properties in other to serve as support systems for bio-integration during skin grafting, repairs, wound healing and subsequent biodegradation. Methods used to fabricate polymer scaffolds for biological systems include freeze drying, electro-spinning, nanotechnology-based fabrication and rapid prototyping. Other techniques used in making scaffolds [23], solvent casting or particulate leaching [21], phase separation [24], gas foaming processing and melt moulding [12]. A blend of techniques may also be adopted in the fabrication of polymer scaffolds. However, recent advances have seen the emergence of ‘bio-

fabrication' technique, which in itself may be defined as production of complex living and non-living biological products from living cells, molecules, extracellular matrices and biomaterials.

4.1.1 Electro-Spinning

Electro-spinning or electrostatic fibre spinning process has become a well-known technique used to fabricate fibres from solution or melt, with dimensions in the nanometre range [9]. Many polymers have been effectively spun into ultrafine fibres and used in biomedical applications. The fibres from electro-spinning have been found very useful in tissue engineering as a result of their inherent properties since they mimic the nanoscale chemical, mechanical and functional properties of extracellular tissues. Nanofibres made via electro-spinning have also found usefulness in textile manufacturing. The process can simply be described as the field electromagnetic drawing of submicron-sized fibres from solution at very high voltage towards a conductive collector or grounded target. The product is usually a sling of filament with size not more than 100 nm in diameter. The filament may be collected, spun into yarn and subsequently made into fabric. When compared to other methods of producing fibres, for example, drawing, template synthesis, self-assembly and phase separation, electro-spinning has the advantage of fibre size control from submicrometres to nanometres. The ultrafine electro-spun fibres are characterized by high surface-to-volume ratios and porosity. It has made the process versatile and very useful in the production of nanoporous textile biomaterial matt or scaffold for extracellular matrices (ECM) in wound dressing and skin regeneration. In other to recover different tissues, including skin, vein, ligament, bone, muscle, tendon and nerve recovery, encapsulating medicinal plant extracts in a polymer solution and electro-spun nanofibres have been employed. Figure 2 is the representative diagram showing the electro-spinning procedure.

In describing the illustration showing the electro-spinning process in Fig. 2, the polymer solution is put into a syringe and pumped, at a controlled rate, through a needle opening. The needle opening is connected to a very high voltage, which induces electrostatic charge to the polymer melt. When the electrostatic charge is stable with surface tension, Taylor's cone is formed and by raising the electric field, fibre jet is discharged from the apex of Taylor's cone. Solvent evaporation takes place as the polymer liquid jet is drawn from the needle opening into ultrafine fibre. The drawing process and solvent evaporation decrease diameter of ensuing fibre from micrometre to nanometre. Finally, conductive metal collector into a cone [9, 19] attracts the electro-spun polymer nanofibre fabricated. The process variables include nature of polymer, polymer solution viscosity, pump pressure, distance between needle and conductive metal collector, and temperature.

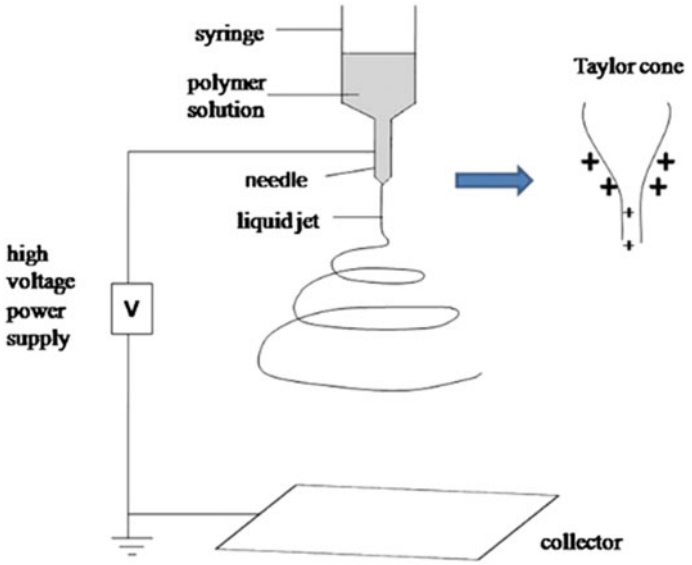

Fig. 2 Schematic illustration of electro-spinning [3]

4.1.2 Gas Foaming

Three-dimensional (3D) template for tissue engineering has been developed using inert gases instead of solvents as the templating phase, while using bioactive polymers in order to obtain scaffolds with highly interconnected polydisperse pores. This is the basis for 3D gas foaming technique for producing bioactive scaffolds. This method may also be regarded as gas-in-liquid scaffold engineering. The process involves first of all using compression moulding to form solid bioresorbable and biocompatible discs of poly (α-hydoxy esters) mixed with salt particles. Poly(α-hydoxy esters) include poly(ε-caprolactone) (PCL), poly(dioxanone) (PDO), poly(glycolic) acid (PGA), poly(lactic-co-glycolic) acid (PLGA), poly(L-Lactide) (PLLA) and poly(D-Lactide) (PDLA). The discs are positioned in a chamber, exposed to carbon IV oxide (CO_2) gas at high pressure of up to 5.5 MPa for 3 days, and gradually reduced to atmospheric pressure. It is possible to obtain templates with 90% porosity and pore sizes of up to 100 μm. The salt particles are then removed by leaching. However, the process set-back is the production of unconnected closed cells. Even though the fabrication technique needs no leaching step and no severe chemical solvents, extreme temperature used in disc formation prevents the introduction of cells or bioactive molecules. Likewise, disparate pore structure causes difficulty in cell seeding and migration within the scaffold.

4.1.3 Solvent Casting and Particulate Leaching (SCPL)

SCPL technique encompasses the dissolution of a polymer in the class of poly(α-hydoxy esters) in an appropriate organic solvent. Particulate salt is blended with the polymer solution and then cast onto a glass plate to produce a membrane or a 3D geometry forming a polymer-particulate salt composite material of some sort. The solvent is then made to evaporate at atmospheric conditions. The polymer-particulate salt composite is then placed in a bath, which dissolves and leaches the salt particles, leaving behind a nanoporous polymer scaffold. This method may be used to prepare porous constructs of synthetic bioresorbable scaffolds with a particular porosity, surface-to-volume ratio, pore size and crystallinity for various purposes by suitable thermal treatment. Scaffolds based on PLLA and PLGA have been produced by this technique, but could also apply to any other polymer that is soluble in suitable solvents with very close solvent interaction parameters. For such cases, carbon tetrachloride and methylene chloride have been used for PLLA and PLGA, respectively.

5 Polymer Hydrogels

Hydrogels are a class of polymers that by their hydrophilic, cross-linked nature, makes them efficient in sucking up tremendous volumes of water without dissolving in it. This is made possible by the chemical and physical properties of the polymer chains. In terms of chemical properties, hydrogels can come in natural or synthetic forms, whereby the former may come from renewable sources while the later may be synthesized from monomers, prepolymers, dendrimers, terpolymers, oligomers or copolymers. In terms of physical properties, hydrogels are highly viscous and cross-linked. For effectiveness as extracellular matrix in biological systems, hydrogels must be biodegradable, non-toxic and biocompatible. This has permitted its boundless ability for its usage in the area of biomolecular recovery and reintegration, pharmaceutics, diagnostics and medicinal services. The main significant impediment of polymer hydrogels is in their mechanical properties which restricts their utilization in numerous other business applications

5.1 Natural Hydrogel (NH)

NH is native pristine hydrogel, which includes natural gums, proteins, peptides, cellulosic materials, collagen, hyaluronic acid and polysaccharides such as schelaroglucan, alginates, cellulose and xyloglucan. Natural hydrogels play a significant role in enhancing tissue regeneration and the central nervous system repair, as it holds the characteristics of mechanical strength and porosity relative to tissue which permits cell infiltration, transplantation and biocompatibility, in the direction of cell attachment, tissue growth and targeted in situ drug delivery.

5.1.1 Chitosan-Based Hydrogel

Composite hydrogels of chitosan laden with zinc oxide are effective for wound dressing to improve wound healing and for quick re-epithelialization. Collagen application on wounds result due to burns, chronic wounds and diabetic foot ulcers. Chitosan-based hydrogels were utilized for sensitive, quick and effective discovery of enzymes and for indirect discovery of bacteria, compatible with infection-sensing and wound dressings.

5.1.2 Polysaccharide-Based Hydrogel

Exclusive properties of polysaccharides create their suitability for the design of biomaterials in respect of their characteristic preferences to manufactured polymers. Existence of functional groups like carboxylic, amine, hydroxyl and sulphate groups, exhibits a lot more extensive degree for their structural modifications for better cell attachments.

A perfect wound dressing material keeps up clammy condition at wound interface, giving a cooling sensation, simple vaporous trade, biodegradability and biocompatibility, permits assimilation of wound exudates, and keeps up obstruction property to small-scale life forms. Polysaccharide-based hydrogels possess these characteristics and make them a good choice for extracellular matrix for wound dressing [1].

5.2 Synthetic Hydrogel

They are man-made hydrogels which found abundant application in medicine. Almost all hydrogels are biocompatible and examined for medical and related products. Example of a synthetic, non-toxic, non-cancerous and biocompatible hydrogel is polyvinyl alcohol (PVOH), which finds its utility in the development of contact lenses, lining of artificial heart, soft tissue replacement, articular cartilage, skin and pancreas. Coordinated discharge of several drugs like ergotamine tartrate was carried out using polyvinyl alcohol.

6 Specialty Polymers for Drug Delivery

In the advancement of drug delivery in biological systems, speciality polymers provide needed support and vehicle for the coordinated discharge of therapeutic agents in cyclic doses, over long periods of time, and tunable release of both hydrophilic and hydrophobic drugs. Drug delivery in biological systems has improved efficiently and effectively through the development of novel techniques to administer complex drugs. The traditional practice of drug delivery by oral or intravenous administra-

tion does not deliver ideal pharmacokinetic profiles particularly for drugs that show great toxicity or slim therapeutic doses. The drug should reach the site of action at a particular concentration and the therapeutic dose range should remain constant over time. However, certain factors mitigate the effective performance of pharmaceutic agents. Such factors include degradation of the drug and its interaction with cells, inability to transfuse into tissues easily due to their chemical nature. Therefore, new formulations as polymeric systems of drug carriers are gaining attention and interest because they can achieve a better pharmacological response. Just as such systems are appropriate tools for distribution and time-controlled drug delivery, the mechanisms involved in drug release require the use of specialty polymers in medicine with a diversity of physicochemical properties, wherein drugs can be encapsulated or conjugated in polymer matrices. These specialty polymeric systems have been used for a wide range of treatments. Various ranges of systems have been produced to accomplish drug delivery utilizing polymers. This assorted variety is an outcome of various drugs forcing different confinements on the kind of delivery system utilized. For instance, a medication that will be discharged over an all-encompassing period in a patient's stomach where the pH is acidic and natural conditions vacillate broadly will require a controlled discharge system altogether different from that of a drug that will be delivered in a pulsatile way inside the blood system [20, 25]. An essential thought in designing polymers for any drug delivery system is the fate of the polymer after drug discharge. Polymers that are normally discharged from the body are alluring for several drug delivery systems. These polymers might be discharged specifically by means of the kidneys or might be biodegraded into little particles that are then discharged. Non-degradable polymers are satisfactory in applications in which the delivery system can be recuperated or expelled after drug release.

For the development of various drug delivery devices, it is essential to observe how the drug released from these devices and understand the mechanism responsible. The drug release from the devices generally depends on the physicochemical properties of the polymers and the physiological medium. The possible factors that can be detrimental for drug release from the polymer are:

- The environment in which the drug is to be released.
- Diffusion from the drug delivery device.
- The chemical (hydrophilic or hydrophobic) nature of the device.

Active targeting mechanisms may be engaged by the polymer carrier, a polymer-drug conjugate or the drug itself to disproportionally partition itself into the tissue of interest.

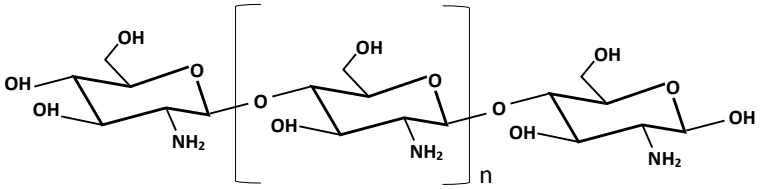

Fig. 3 Structure of chitosan

7 Natural Polymers in Medicine

7.1 Chitosan

Chitosan is a polysaccharide that is obtained from the hard outer skeleton of crustaceans like crabs, clams, shellfish, lobsters, shrimps, periwinkles and snail. A linear polysaccharide is comprised of arbitrarily distributed deacetylated units of *D*-glucosamine and acytelated units of *N*-acetyl-*D*-glucosamine. The natural polymer is formed at about 50%-degree de-acetylation of chitin by treating powder chitin shells of the crustaceans with an alkaline solution like sodium hydroxide. Chitosan is distinctive in its feature. It is a pseudo-natural cationic, hydrophilic and semi-crystalline polymer in the solid state. It is a lot less demanding to be processed than chitin and is also very sensitive to acidic environments. The structure of chitosan is shown in Fig. 3.

Chitosan has a variety of biomedical applications as dietary fibre, antibacterial and drug delivery agent through the skin. It can be processed into scaffolds, bandages, micro- and nanoparticles, nanofibres, micro- and nanogels, films, beads, hydrogels, membranes and sponges [2, 7]. Some derivatives of chitosan are N-methylene phosphonic chitosans, O- and N- carboxymethyl chitosans, chitosan 6-O-sulphate and trimethyl chitosan ammonium.

7.2 Gelatin

Gelatin, a blend of peptides and proteins, is a translucent, faintly yellow, brittle natural polymer. It is derived from collagen obtained from various animal body parts, by denaturing or partial hydrolysis. Parts of the animal skin where gelatin can be simply gotten are white connective tissue or muscles, tendons, ligaments and bones. It responds quickly to dissolution in aqueous solutions of polyhydric alcohol like glycerol, highly polar solvents with hydrogen bonding like acetic acid [10]. Its solubility in hot water when compared to its solubility in ordinary cold water is super. Gelatin has amphoteric properties meaning that it can perform as acid or base. It is extensively utilized in food, pharmaceuticals, photographic industries and various

technical uses. Currently, gelatin is also utilized as a material for producing wound healing scaffolds. This is because gelatin as a natural polymer brings benefits in biomedical applications as biocompatibility, biodegradability and low in cost. There have been recorded successes of gelatin being spun into nanofibers. Ki, Zhang and co-researchers (2005) had effectively produced uniform and very fine gelatin nanofibres utilizing electro-spinning technique [25].

7.3 Shellac

Shellac is a natural resin. Its properties depend largely on the source and the host tree from which it is obtained. It is characterized by drying naturally by air leaving high-gloss sheen. In coatings, it is a choice resin for formulating moisture barrier surface coatings. Shellac-based coatings may be formulated with different pigments/colours. When dried on the substrate, apart from adorning the substrate with colourful outlook, it also leaves behind hard, brittle flakes with or without wax, depending on the purifying process, adhesively held unto the substrate surface. Shellac is tasteless and may have a faint odour.

7.4 Properties

The properties of shellac depend on the insect strain and host tree as well as the method adopted for purifying the crude lac (seed lac).

7.5 Solubility

Pure shellac is soluble in 95–99.5% ethanol and is practically insoluble in ether. White shellac obtained by bleached secretions of Lacciferlacca is sparingly soluble in 95% ethanol and very slightly soluble in ether. Both types are insoluble in water but are soluble in sodium hydroxide solution. Various modified shellacs have been obtained which shows solubility in water.

7.6 Applications

In biomedical applications, thin shellac is widely used as a moisture barrier coating for tablets and pellets because of its low water vapour and oxygen permeability. Usually, it has been applied in the form of an alcoholic solution or aqueous dispersion (pharmaceutical glaze). However, due to stability problems with alcoholic shellac

solutions, it has had limited use in the pharmaceutical industry for modified release or enteric coatings. Recent research results indicate good application properties and chemical stability for shellac films from aqueous shellac solutions. Aqueous ammonium shellac solutions, based on de-waxed orange shellac, do not show the problems exhibited by alcoholic shellac solutions and are used as an enteric coating for pellets, tablets, soft and hard gelatin capsules, primarily in nutritional supplement. Shellac is a primary ingredient of pharmaceutical printing inks for capsules and tablets and can be applied as a 40% w/v alcoholic solution. Other applications of shellac are in the coating or encapsulation of powders or granules in probiotics.

8 Conclusion

Many novel tailored polymers with desirable functional groups are being developed with foreseeable applications in innovative drug delivery systems, in making physiologically friendly linings for artificial organs. Furthermore, they are used in making therapeutic instruments that imitate biological systems such as organs harmed by ailment, mishap or innate irregularities and imperfections. The well-being, viability of the item and accessibility of a steady material, are a portion of the focal points related to utilizing typical human tissues created by in vitro culture procedures. Tissue engineering holds the guarantee of consolidating the advances in culture innovation with the advancement in restorative and surgical intervention, to give new arrangements by implantation of ordinary human tissue that can play out the characteristic capacities for each tissue type. With the advances in polymer synthesis, science and innovation, increasingly characterized, controlled and biocompatible polymers are getting to be accessible. Such polymers will add to new ages of biomimetic nanostructures and vehicles for conveying analytic and imaging specialists, helpful medications, prognostic reagents and multi-operators later on. Along these lines, controlling polymer design for timely and effective drug carriage ought to be a standout amongst the most basic advancements for future drug delivery.

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Chapter 11
Polymeric Nanomaterials for Drug Delivery

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1 Introduction

Polymers are extensively utilized as biomaterials because of their bio-mimetic behavior which makes them biocompatible with biological systems. They are relatively easy to synthesize into a variety of structures and designs in the form of gels, fibrous templates, and soft tissues for the body, to tolerate and recombine. In smart drug delivery discipline, polymers play a substantial part because they serve as carriers for sending therapeutic agents specifically into the proposed site of action, with predominant viability with no adverse or toxic effects. Nanoparticulate delivery systems are designed with effective control of particle size, surface morphology, enhanced infiltration, elasticity, solubility, and discharge of therapeutic active agents so as to achieve the objective and explicit action at a foreordained rate and time. The efficacy of polymeric nanoparticulate systems is effectively achieved in extensive diverse forms. They have proven chemistry, are non-poisonous, biodegradable, and biocompatible. In some cases, nanoparticulate polymeric systems may be said to be "smart" in nature. Accordingly, smart polymers are receptive to climatic upgrade like change in temperature, pressure, and pH, and in this way, they are amazingly useful for focused drug delivery. For example, some polymeric systems when conjugated with antibodies/particular biomarkers, help in recognizing molecular targets

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explicitly in malignant growths. Surface coating with thiolated polyethylene glycol (PEG), Silica-PEG have been known to enhance water solvency and photostability. Surface adjustment of drug conveyance by connecting them with PEG or dextran to lipid bilayer builds their blood dissemination time.

Polymers to be used as drug conveyance ought to be water solvent, non-harmful, and non-immunogenic. They ought to likewise work latently in limiting drug debasement and improving flow time. The safe discharge of the drug is likewise critical. On the off chance that regardless, the polymer is non-degradable, it ought to guarantee that it is not accumulated in body and in the event that it is degradable, the broken parts ought to be with the end goal that they lie underneath renal limit level, non-harmful and ought not create some resistant reaction or adverse effects to the body.

Smart polymers usually display alteration depending on transformation in ecological situations. In biomedicine, stimuli-responsive polymers demonstrate adjustment in properties in light of change in natural conditions. The organic conditions might be hotness, weight, pH, electric field, magnetic field, light, change in attentiveness, ionic strength, and redox potential. Reactions to such stimuli incorporate disintegration, precipitation, swelling, change in conformation, and change in hydrophobic and hydrophilic properties.

Novel polymeric drug delivery systems comprise micelles, dendrimers, liposomes, polymeric nanoparticles, cell ghosts, microcapsules, and lipoproteins. Current progressions in polymer built embodiments and well-ordered drug release frameworks assist in directing drug administration by inhibiting under- or over-dosing, accordingly enhancing bioavailability, limiting side effects and different kinds of burdens caused to the patients [67].

Dendrimers are hyperbranched, monodisperse, 3D molecules of size 1–100 nm macromolecules utilized in delivery of drugs and other therapeutic agents at precise sites. Drug may be encapsulated inside these dendrimers, or may be adsorbed on and conjugated to the surface groups [67]. They additionally go about as carriers, in the treatment of gene. For instance, PAMAM (polyamidoamine) dendrimers are additionally utilized as transporter of hereditary material.

Solid lipid nanoparticles are steady colloidal scheme with solid hydrophobic nucleus which contains circulated or liquefied drug, and also a transporter system in which molten sterol is diffused in water surfactant by microemulsification or elevated pressure homogenization. It can entrap both hydrophilic and lipophilic drugs.

2 Silver Nanoparticles (AgNPs)

2.1 Synthesis of AgNP

Generally, three approaches have been used in the synthesis of nanoparticles. The first is the physical procedures whereby nanoparticles are manufactured by evapora-

tion–condensation utilizing tube furnace at pressure [45, 65]. The benefits of physical procedures are speed, radiation used as reducing agents, and no hazardous chemicals used, but the disadvantages are poor yield and extreme energy consumption, solvent adulteration, and lack of constant distribution [1, 31]. Chemical procedures use water or organic solvents to formulate the silver nanoparticles and have very high yield when compared to the physical method. Natural strategies have been developed as a feasible and green chemistry approach for the production of AgNPs so as to beat the inadequacies of chemical techniques. Biologically mediated production of nanoparticles has appeared to be straightforward, financially savvy, reliable, and environmentally friendly, and much consideration has been given to the high yield production of AgNPs of defined estimate utilizing different natural systems including microbes, fungi, plant extracts, and little biomolecules like nutrients and amino acids as an alternative strategy to synthetic techniques [46, 48, 59, 60].

Silver nanomaterials can be gotten by two techniques, namely "top-down" and "bottom-up" Deepak et al. [24]. The "top-down" technique is the mechanical milling of bulk metals with successive stabilization utilizing colloidal protective agents, Amulyavichus et al. [6], while the "bottom-up" techniques comprise chemical diminution, sol-gel technique, electrochemical technique, and sono-decomposition.

Silver nanoparticles, due to their exclusive and inherent behavior, are viewed as a pioneer in the battle against pathogenic microbial movement. Silver has a solid impact of hindering their movement and impacts down. The increased surface area of silver nanoparticles is an attribute that is accountable for their properties in this respect when compared to the solid silver [79]. This invariably results in better contact with microorganisms, and increasingly successful biocidal action [58]. Silver nanoparticles are known to be viable against an expansive range of Gram-negative and Gram-positive microscopic organisms, including some anti-infection-resistant strains.

Researches have as of late demonstrated that the utilization of silver nanoparticles blended with specific antimicrobials, for example, penicillin G, amoxicillin, erythromycin, clindamycin, and vancomycin, makes a synergic impact in the battle against Escherichia coli and Staphylococcus aureus [3]. Research has likewise proved that silver nanoparticles can be a viable weapon in the battle against infections [80] by hindering their replication. They are additionally not indifferent in specific parasites as researches have demonstrated that they are efficient and quick acting agents that devastate distinctive sorts of organisms, for example, Aspergillus [75], *Candida* [62], and *Saccharomyces*.

2.2 Applications of AgNP

Silver nanoparticles (AgNPs) have some unique properties which have pulled in the consideration of numerous industries, especially those in which a germicide impact is especially alluring like in food, clothing, construction, medicine, cosmetology, pharmacy, and different parts of industry [1, 38].

Antibacterial applications: Silver nanoparticles are incorporated in apparel, footwear, paints, wound dressings, appliances, cosmetics, and plastics for their antibacterial properties.

Conductive Applications: Silver nanoparticles are used in conductive inks and integrated into composites to enhance thermal and electrical conductivity.

Optical Applications: Silver nanoparticles are used to efficiently harvest light and for enhanced optical spectroscopies including metal-enhanced fluorescence (MEF) and surface-enhanced Raman scattering (SERS).

The systems of silver nanoparticles antibacterial movement depends on their normal affinity for bonding with a thiol group that is available in cysteine, which is a building block of the protein bacterial cell wall, in this manner the enzymatic capacity of proteins is irritated and the chain of cellular respiration is intruded. Other enzymes such as the reduced form of nicotinamide adenine dinucleotide (NADH dehydrogenase) and succinate dehydrogenase are also simultaneously devastated.

2.3 Risks Associated with the Use of Silver Nanoparticles

Silver nanoparticles might be viewed as an eco-poisonous biodegradable risk or as an item bio-aggregating in the trophic chain. This has been shown in the report by The US Environmental Protection Agency (EPA) that the entrance of silver nanoparticles into the food chain is conceivable even because of the task of cosmetic formulation containing silver nanoparticles, for example, suntan lotions that can without much of a stretch get into the water. This has been shown to be the quickest way of silver nanoparticles diffusion into living organisms [32]. Current data also revealed how processed nanomaterials mount up in the environment, and how their number significantly build ups on a yearly basis. The widespread use of silver nanoparticles implies that they may infiltrate into nature, polluting water, soil, and air, thereby causing serious harm to the environment. Silver nanoparticles may represent a genuine risk to living creatures inside the biological system. Silver nanoparticles can infiltrate into the human body through the skin, respiratory, and digestive systems. This usually will in general accrue in different organs, particularly in the liver, kidneys, and lungs, prompting negative ceaseless impacts which are probably going to show later on.

3 Plant Extracts for Drug Delivery in Sub-Saharan Africa

Sub-Saharan Africa is home to so many plants with medicinal value. The medicinal value in the plants may be inherent in their leaves, stems, bark, roots, seeds, or fruits. Notable among them are the following [54]:

(i) *Garcinia Afzelli* otherwise called “bitter kola”; its medicinal value is in the fruit and the stem.

(ii) *Aloe Barbadensis*, otherwise called "aloe vera"; its medicinal value is in the leaves.
(iii) *Azadirachta Indica*, otherwise locally called "neem" or "Dogonyaro"; its medicinal value is in the leaves.
(iv) *Zingiber Officinale*, otherwise called "ginger"; its medicinal value is in the root.
(v) Asimina Triloba, *Carica papaya*, otherwise locally called "pawpaw"; its medicinal value is in the leaves and seeds.
(vi) *Moringa Oleifera*, otherwise called "Moringa"; its medicinal value is in the leaves, bark, stem, and seeds.

The inherent metabolites containing bioactive species for effective treatment of ailments may be liquid extracts from plants and shrubs in the form of juice, latex, or colloidal suspensions in water or solvent. Brief explanations of the plants are thus given as follows;

3.1 Garcinia Afzelli (Bitter Kola)

Garcinia kola (*G. kola*), a plant which develops in humid forest, has been unearthed to have numerous applications in conventional medicine, particularly in some African subdistricts. *Garcinia kola*, grown in Nigeria and Ghana, is the most investigated species with all parts studied pharmacologically. Garcinia species possess a wide range of antibody activities, as indicated by recent studies, and this has led to a greater understanding of the pharmacology of various species in relation to antibacterial [28], anti-inflammatory and antifungal [64], antiviral [49], antioxidant [35], anticancer, antimalaria, and other antimicrobial activities [30]. In same vein, several anticancer extracts and compounds from African Garcinia plants have been characterized and their activities against different types of human cancer cell lines also established. It has been alluded to as "the miracle plant" on the grounds that pretty much all aspects of it has been considered and observed to be of therapeutic significance with high nutritional value [73, 77].

Research by Madubunyi (2008) of the ethyl acetate extract of the dried seeds, good antibacterial and antifungal activities were observed against *Bacillus subtilis* and *Aspergillus niger* both at a concentration of 100 μg/ml [69]. Investigation by Adegboye et al. [2], on the methanolic extract of *G. kola,* indicated significant in vitro antimicrobial activities against some bacterial confines including both Gram-positive and Gram-negative living beings tried at a concentration of 20 μg/ml. It was seen that the zones of hindrance shown by the extract against the tested living beings extended somewhere in the range of 10 and 23 mm, while the zones of restraint displayed by streptomycin and tetracycline utilized as standard antimicrobials ranged between 15 and 25 mm and 12 and 25 mm, respectively [2]. Significant antibacterial activities were reported from the water and ethanol extracts of the root bark of *G. kola* in a research carried by Ebana et al. [28]. Research by Iwu [54] also indicates that

the plant extracts have efficacy for significant antioxidative, antimicrobial and anti-inflammatory effects making it a potent medicinal plant.

The antioxidant and scavenging properties of the flavonoid extract of *G. kola* seeds were investigated by Farombi and co-workers. The in vitro assay involved the free radicals and reactive oxygen classes from which the flavonoid extract, known as *kolaviron*, displayed diminishing power and antioxidant activity by impeding the peroxidation of linoleic acid. It was further observed to exhibit 57% scavenging influence on superoxide at a concentration of 1 mg/ml and 85% scavenging activity on hydrogen peroxide at a concentration of 1.5 μg/ml. Furthermore, flavonoid extract, at a concentration of 2 mg/ml, revealed a 89% scavenging outcome on a, a-diphenyl-picrylhydrazyl (DPPH) radical, showing that the extract has efficient behaviors as a hydrogen donor and as a principal antioxidant to react with lipid radicals [35]. Farombi et al. [36], also observed that kolaviron exhibited defensive properties contrary to oxidative impairment to molecular focuses through searching of free radicals and iron binding.

In another study by Farombi et al. [35], the antioxidant and radical searching behaviors were investigated from the flavonoid fraction of the seeds of *G. kola*. The extract was fed to the male rats for six weeks, and their body weights were observed to decrease from 134 to 110 gm/rat. Further studies from the seeds of *G. kola* indicated the methanolic extract to show many activities.

Study by Okoko (2009), on the methanol extract of the seeds of *G. kola*, column chromatographic fractionation under silica gel, and spectroscopic analysis of the active fraction showed the existence of four compounds, viz. garcinia biflavonoids GB1 and GB2, garcinal and garcinoic acids, which were reported to be accountable for the excessive antioxidant capacity of *Garcinia kola* seeds [81].

3.2 Aloe Barbadensis (Aloe Vera)

Aloe vera is utilized in Ayurvedic, homeopathic, and allopathic streams of medicine, including for food, body creams, soap, and medicine. It has been observed to have the capacity to heal sunburns, burns and minor cuts, and even skin cancer. Furthermore, exterior usage in cosmetics mainly performs as skin therapist and averts wounds of epithelial tissues, heals acne, and gives a young-looking radiance to skin, and also performs as exceedingly influential purgative.

The active components of aloe comprise anthraquinones, chromones, polysaccharides, and enzymes. The anthraquinones and chromones are known to be accountable for anticancer activity, anti-inflammatory, and relinquishing [21]. The elements aluminum, barium, calcium, iron, magnesium, sodium, phosphorus, and silicon described to be present in aloe vera gel [21, 41]. The sour yellow sap of the leaves has been observed to encompass byproducts of hydroxyanthracene, anthraquinone, and glycosides aloin A and B from 15% to 40% in diverse researches [17]. Furthermore, the additional effective ideologies of Aloe include hydroxyanthrone, aloe emodin

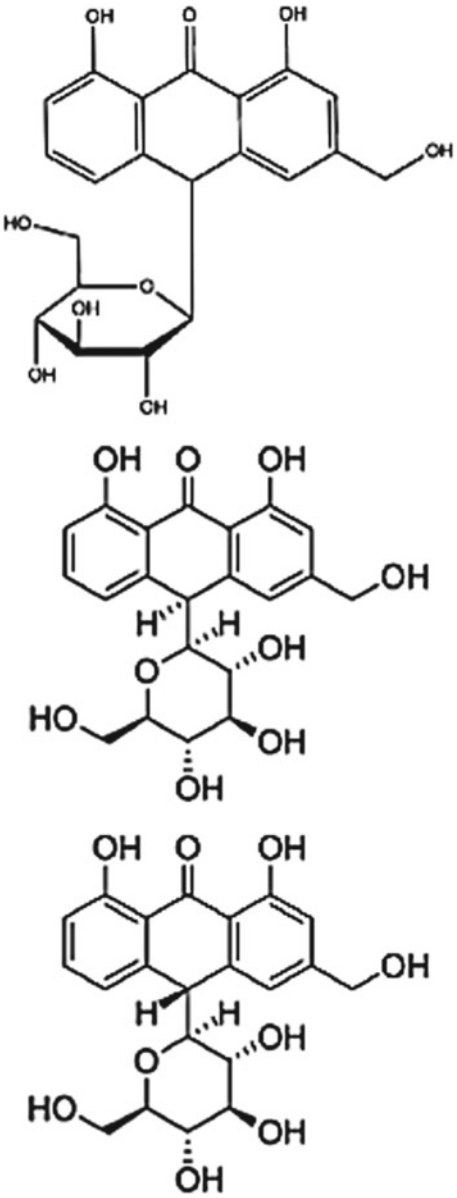

Fig. 1 Structure of aloin, aloin A, aloin B

anthrone 10-C-glucoside, and chromones. Figure 1 shows different aloin structures in aloe vera extract.

The innermost layer of the leaf gel is known to contain water up to 99%, with glucomannans, amino acids, lipids, sterols, and vitamins [16]. The major useful

part of aloe vera is a long chain of acetylated mannose [26, 37, 66], and the gel is frequently commercialized as powder. They are utilized to stop advancing dermal ischemia owing to burns, frostbite, electrical injury, and intra-arterial drug abuse. Moreover, in vivo examination of injuries shows that aloe vera gel behaves as an inhibitor of thromboxane A2, a mediator of advanced tissue mutilation [8].

The injury curative behavior of aloe vera gel has also credited to mannose-6-phosphate [22]. Acemannan which is contemplated as the chief purposeful part of aloe vera is comprised of a extended chain of acetylated mannose [26, 37, 66]. This complex carbohydrate has been observed to hasten injuring curing and reduces radiation stimulated skin reactions [19].

The natural composition and properties of aloe vera are shown in Table 3.1 [23]. The mitigating movement of aloe vera gel is uncovered by various in vitro and in vivo investigations over bradykinase action [20]. The peptidase bradykinase was removed from aloe gel and appeared to separate the bradykinin, which is an inflammatory substance that actuates torment [53]. A novel anti-inflammatory compound, C-glucosyl chromone, has likewise been segregated from the gel extracts [51]. Besides, aloe vera represses the cyclo-oxygenase pathway and decreases prostaglandin E2 creation from arachidonic corrosive. Crisp aloe vera gel was seen to altogether diminish intense aggravation in rodents (carrageenin-incited paw edema), however not in chronic inflammation [20].

The presence of glycoprotein present in aloe vera gel has been discussed to have antitumor and anti-ulcer effects and to enhance propagation of normal human dermal cells [21]. Statistically substantial clinical studies on the efficiency of aloe vera gel on human health are, however, inadequate and usually inconclusive [33]. Aloe vera emodin, an anthraquinone, has been observed to have the aptitude to quash or hinder the growth of cancerous cells, thereby causing it to have antineoplastic properties.

3.3 Azadirachta Indica (Neem)-Dogonyaro

Neem tree belongs to the family Meliaceae which is found in abundance in tropical and semi-tropical countries: India, Bangladesh, Nigeria, Pakistan, and Nepal. Azadirachta indica has complex of various constituents which includes nimbin, nimbidin, nimbolide, and limonoids. These complexes are known to play vital roles in disease management through modulation of various genetic pathways and other activities. Quercetin and ß-sitosterol, which were the first polyphenolic flavonoids purified from fresh leaves of neem, are known to have antifungal and antibacterial activities [43]. Studies on neem extracts have shown that numerous biological and pharmacological activities have been reported [74] including antibacterial, antifungal [63], and anti-inflammatory. Earlier studies and investigators have confirmed their role as anti-inflammatory, antiarthritic, antipyretic, hypoglycemic, anti-gastric ulcer, antifungal, antibacterial, and antitumour [13, 29].

Furthermore, leaf and bark extracts of *A. indica* have also been reviewed for their antioxidant activity, and results of the study show that all the tested leaf and

bark extracts/fractions of neem grown in the foothills have significant antioxidant properties [40]. Study was also performed on the leaves, fruits, flowers, and stem bark extracts from the Siamese neem tree to assess the antioxidant activity, and it was observed that extracts from the leaf, flower, and stem bark have strong antioxidant potential.

Azadirachta indica and their active compounds are observed to play pivotal role in prevention of cancer development and progression, and based on experimentation, it was considered that neem and its ingredients play role in the modulation of various cell signaling pathways.

Another study has been done to investigate the anti-inflammatory effect of neem seed oil (NSO) on albino rats using carrageenan-induced hind paw edema, and it was observed that NSO showed increased inhibition of paw edema with the progressive increase in dose from 0.25 mL to 2 mL/kg body weight. It was observed that at the dose of 2 mL/kg body weight, NSO showed maximum (53.14%) inhibition of edema at 4th hour of carrageenan injection (Naik et al. 2014) [71]. Conclusion from these studies showed that the treated animals with 100 mg kg^{-1} dose of carbon tetrachloride extract (CTCE) of Azadirachta indica fruit skin and isolated ingredient azadiradione showed significant antinociceptive and anti-inflammatory activities [52].

The wound healing activity of the extracts of leaves of *A. indica* and *T. Cordifolia* has been studied using excision and incision wound models in Sprague Dawley rats, and it was observed that the extract of both plants significantly promoted the wound healing activity in both models [14]. Subsequent studies showed that leaf extracts of *Azadirachta indica* promote wound healing activity through increased inflammatory response and neovascularization (Patil et al. 2013).

Aqueous extracts of various parts of neem such as neem oil and its chief principles have antibacterial, antiviral, and antifungal activities as reported by earlier investigators [5, 68]. A study was done to determine the antifungal activity of *Azadirachta indica* L. against Alternaria solani Sorauer, results indicated that ethyl acetate portion was found most efficient in hindering fungal growth with MIC of 0.19 mg, and this portion was also efficient than fungicide (metalaxyl + mancozeb) as the fungicide has MIC of 0.78 mg [55].

Experiment was also undertaken to evaluate the antimalarial activity of extracts using Plasmodium berghei-infected albino mice, and results showed that neem leaf and stem bark extracts reduced the level of parasitemiain-infected mice by about 51–80 and 56–87%, respectively, [4] and other studies revealed that azadirachtin and other limonoids obtainable in neem extracts are active on malaria vectors [25]. As a consequence, there is a growing awareness of the importance of Neem plant in agriculture, industry, medicine and the environment [76].

3.4 Zingiber Officinale (Ginger)

Zingiber officinale (*Z. officinale*), usually known as "Ginger," is regularly utilized spices in universe, which is nurtured for 1000 of years and utilized carefully in

cooking, and medicinally in society and home remedies. It has been utilized broadly in traditional medicine to cure cold, fever, headache, nausea, hypertension, diarrhea, and digestive issues, including being utilized in Western herbal medical practices for treatment of arthritis, rheumatic disorders, and muscular discomfort.

Oleoresin which is the oily resin from rhizomes of Ginger contains several bioactive constituents, such as 6-gingerol, which is main stimulating constituent, i.e., assumed to apply a diversity of outstanding pharmacological and physiological behaviors when used. Antioxidants in ginger include gingerols, shogaols, and some phenolic ketone derivatives. The anti-inflammatory and antioxidant properties in ginger have been known to relieve various inflammatory disorders like gout, osteoarthritis, and rheumatoid arthritis because it offers considerable liberation in discomfort instigated by inflammation and help reduce swelling and morning stiffness [50].

*3.5 Asimina Triloba (*Carica Papaya*)-Pawpaw*

Carica papaya (*C. papaya*), shown in Fig. 2, is a tropical fruit plant commonly called pawpaw in Nigeria, fits to family *Caricaceae*. Papaya is usually recognized for its fruit and dietary value, is a livewire of nutrients, and is accessible all over year. It is a precious source of three antioxidants, namely vitamins C, A, and E. The minerals in *C. papaya* include Mg and K, vitamin B pantothenic acid, folate, and fiber. All the nutrients contained in papaya help to enhance the cardiovascular system, provide protection against heart diseases, heart attacks, strokes, and also prevent colon cancer. The fruit has been observed and reported to be a tremendous source of betacarotene that hindered damage instigated by free radicals that may initiate some forms of cancer. It has assisted in stoppage of diabetic heart diseases by lowering high cholesterol levels being a decent source of fiber [9]. The fermented papaya fruit is an auspicious nutraceutical, an antioxidant, as it recuperates the antioxidant protection in aging patients even without any overt antioxidant deficiency state at the dose of 9 g/day orally.

C. papaya has a pack of enzymes contained in various sections of the plant as shown in Table 11.2. The unripe fruit contains papain and chymopapain. The ripe

Fig. 2 *Carica papaya* tree and fruit

fruit contains β-carotene, carotenoids, crytoxanthin, monoterpenoids, and linalool. The roots contain carposides, the seeds contain papaya oil, glucosinolates, and benzyl isothiocyanate, while the leaves contain zinc (Zn), manganese (Mn), iron (Fe), potassium (K) and some trace minerals. Also contained in the leaves are vitamins C and E, alkalosis and carpaine. The stem contains flavonoids, kaempferol, myricetin, and some minerals including calcium (Ca), magnesium (Mg), and iron (Fe) [57, 61].

The plant, *carica papaya,* has been proven to be used for different medicinal exercises as cancer prevention agent, antihypertensive, injury recuperating, hepatoprotective, anti-inflammatory, antimicrobial, antifungal, antifertility, histaminergic, diuretic, anti-amoebic, antitumor, impact on smooth muscles, antimalarial, hypoglycemic action, immunomodulatory movement, anti-ulcer action, antisickling action. The fluid concentrate of *C. papaya* leaves and roots at various concentration (25, 50, 100, 200 mg/mL) have been accounted for to demonstrate antimicrobial action against some human pathogenic microbes utilizing agar dispersion technique [7].

The latex of *C. papaya* and fluconazole has synergistic impact on restraint of candida albicans development, whose impact results in fractional cell-wall degradation and was accounted for to be in charge of antifungal activity and least protein concentration for delivering a total inhibition at around 138 mg/mL [41].

The extract of *C. papaya* fruit [100 mg/(kg d) for 10 d] for injury-curing property in streptozotocin-induced diabetic rats utilizing excision and dead space injury models has been reported to show 77% decrease in injury area while compared to 59% reduction to injury of controls. This product therefore suggested that extract of *C. papaya* had a strong injury-curing property.

3.6 Moringa Oleifera *(Moringa)*

Moringa Oleifera is one of vegetables of Brassica group and has a place with the family Moringaceae, and furthermore known as horseradish tree or drumstick tree. It contains vitamins A, B, C, and furthermore, rich in minerals, for example, calcium, potassium, and iron. It contains exceedingly absorbable proteins and carotenoids which incorporate β-carotene or provitamin A [27, 34]. Besides being a daily used vegetable traditionally in the West African sub-region, Moringa is broadly known and utilized for its medical advantages. It has earned its name as "miracle tree" because of its stunning recuperating capacities for different sicknesses and even some perpetual illnesses. A few examinations have been completed to detach bioactive compound from different pieces of plant because of its different applications [44].

Due to its phytoconstituents, practically all parts of plant have dietary just as therapeutic properties. In Nigeria, iron content of leaves is beneficial and usually recommended for anemia. Further research has shown that the leaf sources of proteins and sulfur-containing amino acids, methionine and cystine, are usually scarce in the plant kingdom [39].

Owing to antitumor, hypotensive, antioxidant, radio-protective, anti-inflammatory, and diuretic properties of the *Moringa Oleifera* leaf, it is extensively utilized in folkloric medicine. It also has antibiotic, antitryponosomal, hypotensive, hypoglycemic, antidiabetic, and anti-inflammatory activities [42]. The leaves can also be consumed to stimulate metabolism, thus aiding in weight loss.

In vitro and in vivo investigations with plant have suggested its adequacy in treating inflammation, hyperlipidemia, and hyperglycemia [15, 34, 70]. Properties of its phytochemicals, such as flavanols and phenolic acids, were related to the anti-inflammatory, antioxidant, and antibacterial activities [70].

Extracts from Moringa seeds, stem bark, leaves, and root bark are described to have antimicrobial potentials [10]. Onsare et al. (2013) have also stated preliminary work on antimicrobial activity of aqueous extract of pods' husks against Gram-positive, Gram-negative pathogenic bacteria, and yeast strains [78]. Piexoto et al. (2011) reported that in their study, the aqueous and ethanolic Moringa leaf extracts indicated promising potential as a treatment for certain bacterial diseases [56].

Polyphenols, which are naturally occurring antioxidants, are the major plant compounds that are able to decrease oxidative damage in tissues by free radical scavenging and *Moringa Oleifera,* due to its high amount of polyphenols, has been reported to demonstrate antioxidant activity [11].

Moringa Oleifera is outstanding for its pharmacological activities and is utilized customarily for treatment of diabetic mellitus [12]. It has also been revealed to possess potential therapeutic effects to fight cancer, rheumatoid arthritis, and diabetics. Budda et al. [18], observed that *Moringa Oleifera* Lam pod might be a probable chemopreventive agent for cancer. In conclusion therefore, the efficacy of *Moringa Oleifera* in the treatment of some illnesses cannot be over emphasized.

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Chapter 12
Synthesis of Polymeric Biomaterial for Medicine and Surgery

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1 Introduction

Polymer usage as biomaterials is a topic of serious examination in the course of recent years, having made a significant contribution in the present medicinal services innovation. Polymer hydrogels were the first tentatively planned biomaterials for human usage. Their morphology and properties are governed by diverse chemical structure and functional groups, thereby allowing exact regulator of the making of wanted molecular architectures for an extensive scope of applications in the biomedical arena. For instance, biocompatible polymers have been utilized effectively as counterfeit organs and drug delivery systems [1, 2]. The dimension of progress in such applications may be attributed to the self-association and biocompatibility of the defined subatomic design.

The class of biodegradable polymers is the preferred choice for biomaterials and tissue engineering, because of the benefit of avoidable extra medical procedure required to evacuate the inserts or scaffolds, along these lines reducing cost

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and the associated risks involved. However, processing of these biomaterials has posed a major challenge, limiting their use in medical applications. In recent years, there is an ongoing innovative work for the advancement of techniques and equipment for more efficient handling of biomaterials. The application of outcomes of such research and development efforts has led to recorded successes in the treatment of many health-related issues [3–6]. Unfortunately, some biomaterials which have been synthesized for possible use in biomedicine do not have appropriate properties to associate adequately with organic tissues or cells. Be that as it may, it is considered conceivable to improve their intrinsic proprieties utilizing suitable synthesis routes and upscale production techniques for best outcomes. Cross-linking of biopolymers is a method of improving the performance properties of biomaterials for expansive, more demanding medical applications. Extensive research effort has been made around the world, in recent times, to beat the inalienable confinements of current measures of biomaterials and to enhance the biomedical innovation by utilizing three-dimensional (3D) biomaterial scaffold-based tissue engineering (TE) approaches. For instance, the cross-linked form of soft polymers, otherwise called *hydrogels*, another age of animating biomaterials, has exhibited the capacity to develop scaffolds for diverse usages, for example, tissue engineering, deliverance of dynamic particles, and biosensors and actuators [7].

It is essential, in the scaffold-based tissue engineering approach, that the connections of 3D scaffold materials and cells happen by means of biocompatibility, cell grip and proliferation, development, differentiation, and matrix deposition. Scaffolds for tissue building must be planned with suitable surface science and morphology to advance cell capacities and with sufficient basic and physical properties, for example, mechanical properties, porosity, and pore sizes. These scaffolds can be manufactured from the first biodegradable and non-biodegradable polymers. On account of a biodegradable 3D scaffold, it must be planned in such a way that it keeps up basic uprightness, is non-harmful, works adequately, and degrades in a controlled way, until the new tissues are formed and the function proceeds.

There are a few methodologies in tissue engineering at present under scrutiny. A large portion of them use cells, which are seeded onto 3D scaffolds. Scaffolds are frequently intended to be manufactured with an extensive scope of properties which comprise: fitting surface science, porosity measurements from full scale to submicron and interconnectivity systems, which enable cell-to-cell correspondence and relocation, cell multiplication, and separation, lastly to keep up biocompatibility and auxiliary trustworthiness all through the tissue recovery process.

Manufacture techniques for biocompatible 3D scaffolds with proper designs are classified into two divisions: (A) conventional and (B) rapid prototyping. The conventional group of production techniques regularly does not give adequate physical and mechanical properties, and thus, such kinds of scaffolds experience twisting on account of cell motility. The rapid prototyping strategies, then again, do not have such weaknesses and can give every fundamental trademark to particular tissue engineering application. Three-dimensional nano-/miniaturized scale design scaffolds that were manufactured by speed prototyping demonstrated a critical effect on cell mor-

phology, cell expansion, and differentiation, furthermore on the working of different cell types [8–10].

3D surface patterns made by photolithographic procedure, can control cell conduct and communications, among themselves and with the polymer grid [11–15] because it provides restricted geometry along with lateral structures for cellular adhesion. Karp et al. [16] have employed a photolithographic process to create 3D pattern surfaces using chitosan. They displayed the age of 3D designed surfaces of different polymers by coating a thin layer of photo-cross-linkable chitosan on a glass slide. Heart fibroblasts were refined on these designed surfaces which formed stable patterns for as long as 18 days of the way of life period. A few specialists have additionally demonstrated that when cardiomyocytes were refined in paths designed with 68–99-mm width, it indicated articulation of heart troponin I and responsiveness toward electrical field incitement.

Epitome of hepatocytes inside polyethylene glycol (PEG) diacrylate hydrogel through photograph-incited designing, yielded around 21,000 cell groups for every 100 mm^2 gel as a living cell cluster with exact control of cell situating, in which length of cell reasonability was up to half month. Photolithographic frameworks anyway still have a few difficulties which have not been examined, for example, economic viability of the production procedure, the absence of goals, the absence of unique properties following the production of patterns, and inadmissibility of bright beam touchy organic materials for pattering.

There are various points of interest of creating a reasonable 3D structure by the self-organization strategy, which incorporates (i) the age of structures under physiological conditions, (ii) non-attendance of poisonous synthetics or initiators, and (iii) non-appearance of high temperature for restoring. A self-association strategy could hence be utilized in various biomedical applications.

The 3D honeycomb structure of scaffolds has been exhibited in numerous research articles [17–22], to have a solid effect on cell multiplication, cytoskeleton, focal adhesion, and extracellular protein generation. Scientists have likewise discovered that pore sizes of the scaffold have a substantial impact on gene regulation. Investigations on the development of malignant growth cells on the 3D honeycomb surface were likewise directed by a few scientists in late time. It was discovered that the development of such malignancy cells was much lower when contrasted with that of a control 2D surface.

1.1 3D Scaffolds by Self-assembly Peptides

Peptides are normally blended biopolymer constituents. They are produced from the arrangement of amino acid monomers that convey a carboxyl and an amine functional group on chain. They are produced from both natural and synthetic amino acids, which are connected together to form short peptides and afterward long polypeptide chains in a controlled way [23]. The amine (–NH) and carbonyl (–CO) functional groups present in the peptide chain enables further chemical reactions executed with

such other functional group as thiols and alcohols, and these could be joined with a broad scope of resources as lipids, sugars, nucleic acids, and metallic nanocrystals [24]. Peptides have superb bioproperties, for example, biocompatibility, protection from extraordinary states of high and low temperatures, cleansers, and denaturants [24], in this manner making them equipped for a wide scope of chemical interactions and molecular acknowledgments, producing different non-covalent reactions in water, plus hydrogen holding, ionic, p–p associations, hydrophilic and hydrophobic. These interactions in this manner prompt the development of supramolecular self-assemblies that can result in diverse forms of 3D nanostructures, for example, nanofibers, nanotubes, and nanoparticles [25, 26].

Critical innovations are made on self-assembly peptides (SAPs) over the most recent two decades and keep on extending quickly worldwide as a key piece of nanostructure age [23, 27]. Their wide scope of utilizations comprises of drug delivery, nano-biotechnology, and nano-electronics in tissue designing. SAPs with low-atomic weight peptides (oligopeptides) are equipped for making microenvironments for cell culture [28, 29] and tissue recovery [30, 31]. Holmes et al. [32], have demonstrated that SAP nanofiber scaffolds can advance optic nerve recovery. SAP nanofiber frameworks which are formed suddenly from individual peptides by interfacing with physiological salts are completely biocompatible. It has additionally been exhibited that SAP hydrogel is a possible scaffold for biosynthesis of extracellular matrix (ECM) and glycosaminoglycan (GAG) buildup within a 3D cell culture for ligament tissue fix.

2 Synthesis of Polymer Hydrogels

Hydrogels or “swell gels” are 3D structured polymeric materials, formed via cross-linking reactions of polymers. Hydrogels may be synthesized for a particular biomedical application with prerequisite properties relying upon the compound structure, composition, and confirmation of preliminary materials, density, hydrophobicity, and hydrophilicity. The 3D structural integrity and properties of hydrogels are for the most part subject to their synthesis technique, for example, physical or compound cross-linking response [1, 2]. Hydrogels from substance cross-linking structure form permanent junction-type networks, like polymerization of the acryloyl group, ionizing radiation-initiated cross-linking (photo-polymerization), small particle cross-linking with a polymer chain (glutaraldehyde), and polymer–polymer cross-linking by a compression reaction. Though physical cross-linking of hydrogels permits the formation of transient intersection-type networks, for example, chain entanglements or physical collaborations, for instance, ionic interactions, hydrogen bonds, or hydrophobic associations.

Hydrogels might be incorporated from characteristic and engineered polymers. Instances of hydrogels from normal polymers incorporate collagen, gelatin, hyaluronic corrosive, chondroitin sulfate, chitin and chitosan, and their subsidiaries. Hydrogels from normal polymers have numerous focal points over artificially

inferred hydrogels, for example, low harmfulness and great biocompatibility, because of their chemical structures. They have structures like glycosaminoglycan (GAG) atoms present in the local extracellular lattice (ECM).

Hydrogels from synthetic polymers are formulated by polymerization reaction procedures utilizing appropriate preliminary monomeric units. Samples are those acquired from acrylates, methacrylates, and so on [33].

Electro-responsive frameworks have been created utilizing hydrogel matrices where pulsatile discharge profiles are procured with the on/off utilization of an electric field [34–37]. Investigations on the distortion of polyelectrolyte gels affected by an electric field were accounted for by Shiga and Kurauchi [38].

Deformation happens in three distinctive ways—swelling, contracting, and bending—which relies upon the ion concentration in the gel when the electric field is connected to the hydrogels. While the gel shrivels at low ion concentration, it swells at high ion concentration. In addition, a gel in the form of a strip displays flexural behavior [38], whereby the flexural direction is subject to the type of ion. The flexural mechanism and water uptake behavior of polymer gel are explained by the Flory–Huggins theory of osmotic pressure [39].

Kim et al. [40] also investigated and stated the electrical response characterization of chitosan/polyacrylonitrile hydrogel at various concentrations of NaCl aqueous solutions and observed that the IPN hydrogel displayed electrical-sensitive behavior and the equilibrium bending angle (EBA) gotten to a peak at 0.9 wt% of NaCl concentration, and there was a decrease in the value at greater levels. One of the best studies in the electro-responsive hydrogel field was carried out by Xiang et al. [41], who tried to find out the electro-responsive behavior of sulfoacetic acid modifying PVA hydrogels. Owing to the lack of electrolyte groups in the PVA hydrogel, they observed that it was important to bring some ionizable groups into it so as to make the hydrogel electro sensitive. They also studied swelling and mechanical properties of the hydrogel and concluded that hydrogel swelling increased with a decrease in the ionic strength of the solution.

It is worthy to note that the mechanical behavior of electric field-sensitive hydrogels is very essential, since the material is expected to withstand recurrent forces. If not, the structure of the hydrogel will deteriorate over a period of time and complete breakdown. This is not a desirable behavior in applications that should exhibit utmost resistance to tensile, flexural, and compressive forces, in other to preserve the structure of the hydrogel drug carrier. On the contrary, if the hydrogel structure fails in mechanical properties, it would hinder effective drug release/delivery. When the hydrogel is used as a drug delivery system, it exhibits a poor mechanical property and breakdown effortlessly. But, in other to surmount this problem, hydrogels should be strengthened so that their mechanical properties are preserved.

3 Synthesis of Furan-Based Polymer

Furan-based polymers are a class of polyesters synthesized from polysaccharides producing renewable plants. Some of the very important organic compounds which may be synthesized from glucose, fructose, and cellulose are the furan dicarboxylic acid (FDCA) precursors, which are symmetric heterocyclic diacids obtained from the oxidation of both primary alcohol and aldehyde groups of hydroxymethylfurfural (HMF), in the presence of gold, cobalt, chromium, or platinum catalysts [42]. The 2, 5-furan dicarboxylic acid (2, 5-FDCA) monomer, a "YXY" building block as shown in Fig. 1, is a typical example of a symmetric diacid. The compound has two carboxylic acid groups that make it a suitable reactant with diols or diamines in a polycondensation esterification reaction.

Previous studies had reported that instead of causing 2,5 furan dicarboxylic acid to react with a diol such as ethylene glycol (EG), it may be reacted with a tri-, tetra-, penta-, and hexamethylene diol, to yield several polyester resins as polyethylene 2,5-furandicarboxylate, polypropylene 2,5-furandicarboxylate, polybutylene 2,5-furandicarboxylate [44, 45], with different properties meant for different applications. One of such derivatives is polyethylene furanoate (PEF) obtained from the step-growth polycondensation reaction of 2,5-FDCA and EG. PEF is a better bioplastic material because it has better barrier properties and thermal stability than polyethylene terephthalate (PET) used for food packaging [46, 47].

Furthermore, obtaining a furan derivative for self-healing applications in regenerative medicine may be achieved through various routes. Zeng et al. [48] reported the preparation of a furan-based polymer, poly(2, 5-furandimethylene succinate), synthesized via polycondensation reversible Diels–Alder reaction amid furan and maleimide groups. This permitted the creation of network polymers cross-linked by a bismaleimide. By regulating the mole ratio of the bismaleimide to furan, the mechanical properties of the biomaterial were varied widely. When tested, the material exhibited exceptional self-healing property without external stimulus [48]. Liu and Chuo [49] reviewed the synthesis of a number of self-healing furan-based polymers. Gomes et al. [50] and Gandini et al. [51] have also given an account of several

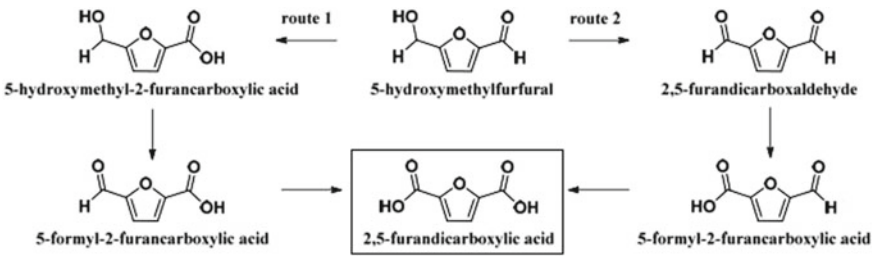

Fig. 1 Synthesis routes for 2, 5-FDCA through the aqueous oxidation of HMF in the presence of a gold catalyst [43]

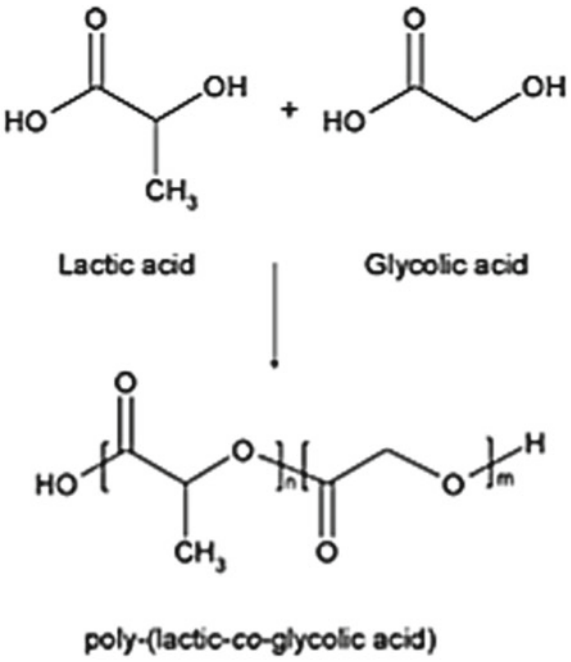

Fig. 2 Chemical structure of poly(lactide-co-glycolide acid) and its monomers [52]

polymers synthesized with 2, 5-FDCA and various diols, and several other types of research are ongoing.

4 Synthesis of PLGA Fibers

Poly(lactide-co-glycolide) acid (PLGA) copolymers represent a critical group of polymers for biomedicine. They are biocompatible and biodegradable, degrading in vivo to harmless items. At times, foreign body reactions on in vivo implantation can be limited via cautious control of polymer properties which incorporates purity or degradation rate. Poly(lactide-co-glycolide) acid (PLGA) properties can be custom-made for the specific application by essentially changing the lactide–glycolide proportion or potentially lactide diastereo-isomeric structure. Poly(lactide-co-glycolide) application in controlled drug delivery and orthopedics has developed enormously over the most recent two decades and is relied upon to become further in the years to come [52].

PLGA is a linear copolymer which can be produced at various weight fractions amid its constituent monomers, lactic acid (LA) and glycolic acid (GA) as shown in Fig. 2.

Enzymatic polymerization technique is the technique that shows up as an alternative strategy to getting aliphatic polyesters uncontaminated with conceivable poisonous metallic deposits, that is a basic right to combine a material for biomedical applications. This component of enzymatic ring-opening by lipase happens under gentle response conditions (temperature, pH, and weight), yet it requires a long response time, creating PLGA with a low molecular weight [53].

Ultimately, by ring-opening polymerization procedure, atactic or syndiotactic poly(lactic-co-glycolic acid) (PLGA) biodegradable material is synthesized randomly as revealed by Dechy-Cabaret et al. [54]. This relies upon the proportion of the two monomers, lactic acid (LA) and glycolic acid (GA), used for the reaction, the end-product application and / or the reason for the polymerization reaction. According to the literature, the PLGA sequence drastically affects the degradation rate, because random PLGA degrades faster than analog-sequenced PLGAs, produced by ring-opening polymerization. Modern technique to acquire repeating sequence PLGA copolymers with diverse tacticities has recently been suggested by Li et al. [55], using 1, 3 diisopropylcarbodiimide (DIC) and 4-(dimethylamino) pyridinium *p*-toluenesulfonate (DPTS) as catalysts.

LA and GA are formed as by-products after degradation. The degradation rates can likewise be affected by various parameters such as the molecular weight, the ratio of GA to LA, stereochemistry mixtures of D and L lactic acid monomers, and end-group functionalization.

A distinct advantage of PLGA copolymers is that they may be fabricated to have anticipated properties making it possible to have a material with a broad spectrum of functioning characteristics gotten by thorough maneuvering of three crucial properties of the copolymer, viz. composition (lactide–glycolide ratio), lactide stereoisomeric composition (L- or DL-lactide), and molecular weight (MW). Figure 3 shows different schemes for the polymerization of PLGA.

Numerous researches have revealed that PLGA insert in bone or soft tissues of animals trigger off none or only a minor inflammatory reaction, which lessens with time [57–59]. So far, no toxicity or allergic responses have been reported or observed.

5 Synthesis of Poly(lactic) Acid (PLA) Fibers

PLA is a natural biopolymer. Presently, it is a standout among the encouraging biodegradable polymers (biopolymers) and has been the focus of inexhaustible writing in the course of the most recent two decades. The polymer has a place with the group of aliphatic polyesters [47]. It is one of only a handful couple of polymers in which the stereochemical structure can without much of a stretch be adjusted by polymerizing a structured blend to produce high molecular weight and semicrystalline polymers. PLA can be prepared by means of countless techniques and is industrially accessible from large-scale manufacturing plants, in a moderately low cost and wide scope of grades with exceptional properties. This makes PLA appropriate for diverse applications. Its biodegradability is adjusted to short-term packaging, and its

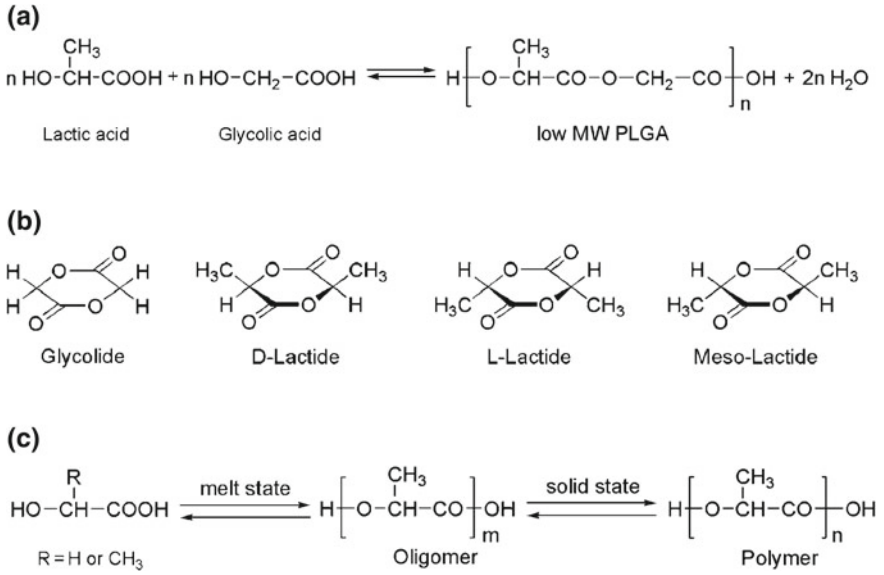

Fig. 3 **a** Polycondensation of lactic and glycolic acid, **b** structures of glycolide and lactide, and **c** melt = solid polycondensation of lactic and glycolic (R¼H) acid [56]

biocompatibility in contact with living tissues is utilized for biomedical applications, for example, inserts, sutures, frameworks, and drug encapsulants. Classification of biodegradable polymers is shown in Fig. 4.

Properties of PLA can be enhanced through the variation of isomers (L/D proportion) and the homo and (D, L) copolymer relative substance. Furthermore, PLA can be custom-made by presenting plasticizers, different biopolymers, and fillers amid its formulation. PLA is both biodegradable and biocompatible when in contact with living tissues for biomedical applications, for example, inserts, scaffolds, sutures, and drug encapsulants. PLA can be degraded by abiotic degradation which is a basic hydrolysis of the ester bond without requiring the nearness of enzymes to catalyze it. Amid the biodegradation procedure, and just in the second step, the catalysts degrade the remaining oligomers till final mineralization. This happens in as much as the essential monomers (lactic acid) are generated by fermentation from renewable resources (carbohydrates). The production of PLA is a multistep procedure which begins from the generation of lactic acid and ends with its polymerization [61–65]. The production of PLA can follow three main routes as shown in Fig. 5.

Lactic acid is condensation polymerized to produce a low molecular weight, brittle polymer, which is usually unusable, except if external coupling agents are utilized to build its chain length. The second process is the azeotropic dehydrative condensation of lactic acid which can yield high molecular weight PLA without the utilization of chain extenders or extraordinary adjuvants [63]. The third procedure is ring-opening

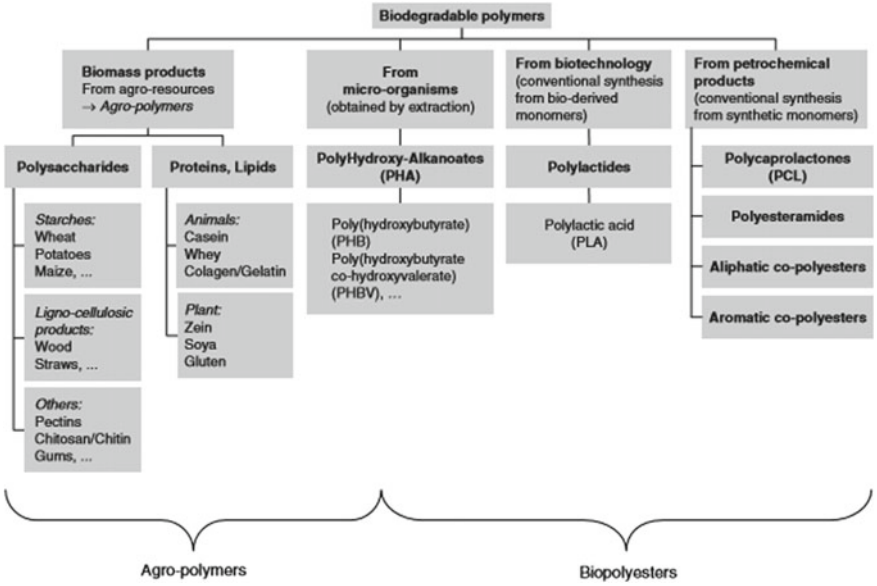

Fig. 4 Classification of biodegradable polymers [60]

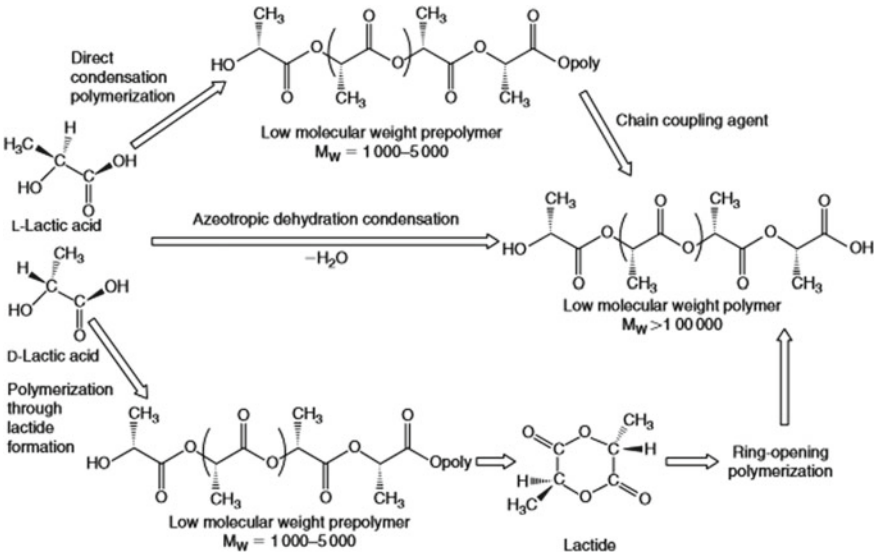

Fig. 5 Three major ways for the production of PLA [66]

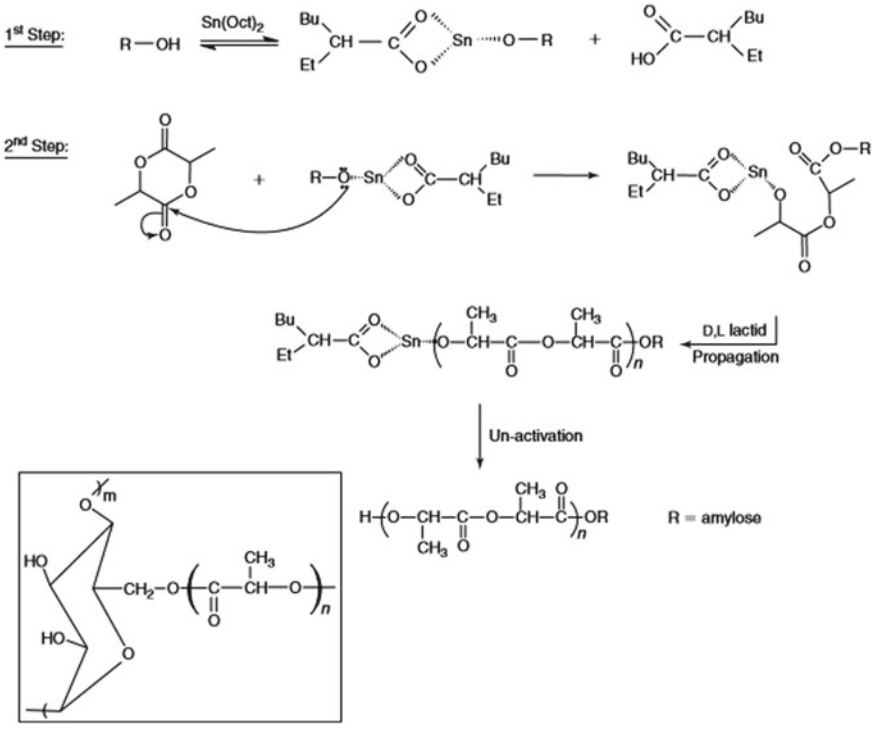

Fig. 6 High molecular polylactic acid synthesis technique [66]

polymerization (ROP) of lactide to acquire high molecular weight [67] as appeared in Figs. 5 and 6.

6 Synthesis of Biocellulose Fibers

Cellulose is the most bounteous, cheap, and promptly accessible starch polymer on the planet, generally separated from plants or their squanders, with structure shown in Fig. 7.

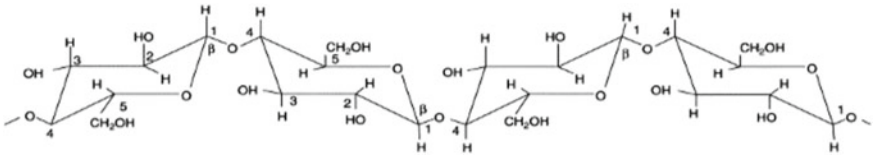

Fig. 7 Structural formula of cellulose

Cellulose is one of the important clusters of biomaterials due to its unique physical and chemical properties; its fibers are being utilized as possible strengthening materials on account of numbers of points of interest which include its abundance, low weight, biodegradability, cheapness, renewable, low abrasive nature, interesting by-products from waste biomass, and good mechanical properties. Plant cellulose is most commonly used in pulp and textile industries. However, it is not pure. It contains many contaminants, hemicellulose and lignin, which requires rigorous chemical treatments to remove most of the impurities. The chemical purification of plant cellulose usually results in irreversible alterations of its structure, which eventually deprive the polymer of its advanced characteristics, thereby negatively impacting its functionality in advanced applications.

Biocellulose, a polymer produced by *Acetobacter xylinum*, has been a high-esteem biotech item, otherwise called a polymer with high strength and one of the kind structures making it a decent biodegradable biopolymer. Biocellulose (BC) is a 100% unadulterated type of cellulose nanofibers that comprises of higher basic crystallinity and a higher level of polymerization [68, 69]. This exceptional pure structure helps it to attain the novel physical and biological properties, for example, malleability, high rigidity, oxygen porousness, biocompatibility, and biodegradability [70].

These superior properties of biocellulose make the biopolymer an exceptionally potential precursor for leap forward innovations in membrane engineering, green biotechnology, and hybrid nanocomposites [71], which eventually would prompt cutting-edge application and products, such as man-made skin, vein substitute, bone scaffold, and electromagnetic papers. Considering these inherent properties, the high-scale production of biocellulose would favor it as a superior replacement to plant cellulose in a wide scope of use in our regular daily existence [72].

Production of biocellulose is usually achieved by Acetobacter bacterial varieties in the presence of carbon and nitrogen sources in the fermentation medium [68, 73]. Regular techniques for biocellulose generation use different kinds of sugars as a carbon source. Fructose, glucose, sucrose, and xylose have been more than once utilized in the generation of BC by *Gluconacetobacter xylinus* microorganisms in both static and agitated cultures, and in numerous diverse reactor configurations [73–75]. The bottleneck in scaling up biocellulose production using these feedstocks rests in their high economical cost and moderately low production yield. This has led to several attempts with alternative feedstocks being investigated to increase the production yield of biocellulose and reduce the economical cost [76–81].

As a renewable polymer, cellulose is obtained from fibrous plants, soft and hardwood, and shrubs. Corn roots, mung bean hypocotyls, radish roots, and coleoptiles are plants well known to produce cellulose. Land plants such as mosses, amoebae, ferns, certain fungi (the Oomycetes), angiosperms and gymnosperms, cellular slime molds (*Dictyostelium discoideum*) and a great diversity of algae (*Vaucheria*, *Glaucocystis*, *Pleurochrysis*, *Oocystis*, *Valonia*, and *Eremosphaera*), plankton and marine algae also have the ability to produce cellulose [82]. In addition, a wide variety of living organisms are also capable of producing cellulose.

Xylinum is the most agreed on biocellulose producer in terms of efficiency and the most studied in the literature. They are mainly called *A. xylinum*, *A. xylinus*,

A. aceti ssp., and *xylinum*. *A. xylinum* is a wellspring of carbohydrates among the supplements that assume a key job in the fermentation procedure for the synthesis of cellulose; as a result of this, *A. xylinum* makes glucose as the energy source [80, 81].

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Chapter 13
Synthesis of Bio-Based and Eco-Friendly Nanomaterials for Medical and BioMedical Applications

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1 Introduction

The crossing of paths of sciences of biomedical and nanotechnology has opened a wide variety of research endeavors at molecular and cellular levels. Since biosynthesis of nanoparticles is a relatively economical and ecologically friendly sound substitute to conventional biological and natural synthetic techniques, green chemistry of this fascinating synthesis of nanoparticles has elicited significant interest and considerable development has been recorded. In some instances, these green approaches of synthesizing NPs can be achieved at: low costs, ambient temperatures, neutral pH and of course, in an environmentally friendly fashion. In view of these considerations, nanomaterials can be synthesized by employing various routes, among which are biological alternatives, plants and plant extracts appear to be best options, even though other biological routes, such as: fungi, bacterial, are available. This is because, plants are naturally nature's chemical factories needing low maintenance and of course are in abundance and very cost effective.

Various techniques, e.g., physicochemical and organic methods have been created with the end goal to fabricate nanoparticles with precise profiles. Productions of nanoparticles via natural and biological procedures, often, are costly and dangerous chemicals may be required. However, advancements in green production of nanoparticles, comparatively to natural and biological means, confer environment-friendliness, just as the methodologies are economical and modest. The production of nanoparticles by exploiting: microorganisms, yeasts and viruses; phototrophic eukaryotes comprising vegetables, phytoplankton as well as algae; heterotrophic human cell lines and some other organic agents, is experiencing significant interest in science community. These nanomaterials find applications in various fields,

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ranging from sensors, medical biology, drug delivery, labeling, environmental cleanup and dentistry.

Parveen et al. [33] succinctly reviewed the assorted variety of field, beginning with historical background of nanotechnology, properties of nanoparticle and different techniques for the production, culminating in different benefits and drawbacks of various strategies of synthesis and their applications. Ullah et al. [48] reported on the ongoing progressions in biofabrication, in light of microorganisms from nano to mesoscopic dimension, infections to genuine organic organisms, prokaryotes to eukaryotes and from unicellular to multicellular organisms. Microorganisms, as biotemplates, can be used for production of innovative bionanomaterials, microdevices, and miniaturized scale/nanorobots and so on through the use of different base up methodologies. They reviewed the function of: bacteria, microscopic organisms, fungi and green growth as basic layouts in bioproduction of different bionanomaterials for various purposes and gave novel bits of knowledge to future advancement of manufacture innovation by utilizing these microorganisms.

1.1 Production of Silver Nanoparticles

The unique properties of silver nanoparticles enable them to find varied applications in several fields. They are highly potent for their activities, such as: anticancer, catalytic, antimicrobial, larvicidal and wound healing activities, in the medical and biomedical fields. Enormous momentum is deplored, in the biogenic syntheses of silver nanoparticles by utilizing plants and their pharmacological and other useful applications, are on the rise. From time immemorial, silver has been utilized in

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various ways to treat burns, wounds and a numerous diseases triggered by pathogenic microbes. A lustrous transition metal, silver is a soft, white metal that possesses elevated electrical and thermal conductivity. For centuries, this metal is known for its undeniable medical and therapeutic benefits, long before the realization that microbes are agents for infections. Its domestic use includes: vessels, sutures, coins, solutions, foils and colloids as lotions, ointments, etc. Of course, in medicine, it is foremost therapeutic agent for infectious diseases and surgical infections. Therefore, the benefits emanating from silver are more than the risk factors.

Because of the emergence of multidrug-resistant bacteria, silver nanoparticles (AgNPs) have found considerable interest as a category of antibacterial agents. However, the toxicity of chemicals involved in the commonly employed chemical methods for the synthesis of AgNPs presents limitations for subsequent pharmaceutical and biomedical applications. Jun et al. [22], reported on the utilization of 70% aqueous ethanol extracts of *Polygala tenuifolia* root to reduce Ag^{+} ions for the synthesis of AgNPs (Ag°). They characterized the synthesized Ag° with UV-Visible spectrophotometry, transmission electron microscope (TEM), atomic force microscope (AFM), X-ray diffractometer (XRD) and noticed a resilient surface plasmon resonance band at ~414 nm. They concluded that TEM and AFM analyses showed globular and showed globular and irregular shapes of the Ag° synthesized and that XRD data confirmed crystalline description of AgNPs, having crystal size of ~15.12 nm. They concluded that AgNPs synthesized, exerted the most astounding antibacterial action against, *Escherichia coli* among the verified Gram-positive and Gram-negative microscopic organisms and this procedure can easily be scaled-up in order to produce of AgNPs for applications in treatment of bacterial contaminations.

Khan et al. [25] reviewed the diverse types of fungi that were employed for biosyntheses of AgNPs metal nanoparticles, their characterization and potential biological usages in areas, such as: wound restoration, pathogen discovery and regulator, food conservation, textiles, fabrics, and so on. They synthesized AgNPs by utilizing fungi with extreme monodispersity, precise composition and a constricted size range and that among the distinctive organic strategies utilized for metal nanoparticle production, fungi are viewed as an unrivaled biogenic technique, attributable to their decent variety and better size control. They concluded that green, straightforward and successful methodologies are suitable for biosynthesis of AgNPs, which are imperative in view of their lesser poisonous quality and naturally agreeable conduct. They further made attempts to comprehend the biosynthesis of AgNPs by utilizing different fungi and assess their prospective functions as: antimicrobial, antibacterial, antifungal, antiviral, antidermatophytic, antitumor, hepatoprotective, cytotoxic, hypotensive and immunomodulatory activities of these AgNPs. They concluded that the production of AgNPs by utilizing fungi is a hygienic, green, economical, dependable and nontoxic technique which can utilized for variety of usages in reality.

Dipankar and Murugan [6] studied the production and properties evaluation of silver nanoparticles by utilizing *Iresine herbstii* and assessment of their antibacterial,

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cell reinforcement and cytotoxic movement. They reported that the response blend changed to tanish dark color, following seven days of gestation and shows an optimum absorbance of about 460 nm normal for Ag nanoparticle. They concluded that SEM/EDX analysis revealed pure and polydispersed silver nanoparticles and particle size spans between 44 and 64 nm. XRD investigations showed that the greatest of nanoparticles produced, were of cubic and face centered cubic crystals, in shape. In addition, they inferred that FTIR-revealed nanoparticles were crowned with plant compounds and that biosynthesized silver nanoparticles revealed strong antibacterial action contrary to human pathogenic bacteria. They further concluded that phytosynthesized nanoparticles displayed robust antioxidant activity. They concluded that the method of green synthesis is economical, ecological and can be a substitute to orthodox techniques of silver nanoparticles synthesis. They concluded that silver nanoparticles synthesized displayed powerful bioactivity which leads to medical use as an antibacterial, antioxidant and cytotoxic agent.

Anand et al. [1] synthesized bio-based silver nanoparticles by utilizing the filtrate of contagious type of marine dregs of Southern Peninsular beachfront area of India and they identified, based on sequence analysis of Internal Transcribed Spacer, the region of rRNA genes.

They acknowledged the species as: *Aspergillus flavus SP-3*, *Trichoderma gamsii SP-4*, *Talaromyces flavus SP-5* and *Aspergillus oryzae SP-6*. They compared phylogenetic bond amid fungal segregates and other fungal strains. They concluded that treatment of silver nitrate with fungal extract formed steady, prevalent, monodispersed and globular silver nanoparticles. Characterization of isolates showed that nanoparticles span between 20 and 60 nm in entire fungal isolates. They concluded that of all fungi, the silver nanoparticles of *T. gamsii SP-4* displayed an improved antimicrobial activity contrary to Gram-positive bacteria, Gram-negative bacteria and fungi pathogens, an antioxidant activity at an actual concentration of 99 μg/ml and a dose reliant on cytotoxic activity against HEp2 cell lines at LC50 value of 23 μg/ml. They, therefore, recommended that strains: *SP3*, *SP4*, *SP5* and *SP6* can be utilized for simple, harmless and effective production of antimicrobial and HEp2 cytotoxic silver nanoparticles.

1.2 Biosynthesis of Gold Nanoparticles

Sardar et al. [41] succinctly reviewed the past, present and future of gold nanoparticles. Their review considered the current advances in synthesis, electrochemistry and optical properties of gold nanoparticles, with prominence on information originating the development and with an eye to their outcomes. They reported that important features of Au nanoparticle synthesis encompassed the two-phase synthesis of thiolated nanoparticles, the confiscation and diminution of Au salts within dendrimers, the controlled development of bigger particles of very much characterized shapes through the existing methodology, and the gathering of an assortment of nanoparticle systems and nanostructures. They managed on the undeniable reality that electrochemistry

of thiolated Au nanoparticles is systemized as locales of mass continuum voltammetry, voltammetry intelligent of quantized twofold layer charging and molecule like voltammetry intelligent of subatomic energy gaps and that these highlights are essentially dictated by the nanoparticle core. Fascinating multielectron Au nanoparticle voltammetry is seen when the thiolate ligand shell has been enriched with redox groupings. They highlighted further, a fact that the development of Au nanoparticles was discovered in order to display the unexpected properties, like: dissimilar catalysts, beginning with low-temperature oxidation of CO. They concluded that significant progress has been done in comprehending the surface plasmon spectroscopy of Au nanoparticles and nanorods and that the necessity to explore the photosensitive properties of metal particles of a solitary, very much characterized shape and size, has prompted the improvement of various new strategies, prompting the investigation of electron exchange and redox catalysis on single nanoparticles. Drug delivery and numerous biomedical applications necessitate the immense interest in the application of nano-colloids for photo-thermal ablation. As a result of its low toxicity, gold has been particularly employed. Resulting from the fact that the surface plasmon reverberation mode is animated with light, there is the necessity of the pinnacle absorbance in the close infrared where natural tissue transmissivity is utmost. Kereselidze et al. [24] reported on the physical, chemical and optical performance of nanoscale colloids that rely upon their material composition, size and shape. It is appropriate to realize that the characteristics of metal nano-colloids are that they can have a solid surface plasmon reverberation and that the pinnacle of the surface plasmon reverberation mode relies upon structure and creation of metal nano-colloids. They described a method for synthesis of star-shaped colloidal gold. The technique depended on an answer comprising silver seeds that are utilized as the nucleating operator for anisotropic development of gold colloids. They carried out a SEM examination on the subsequent gold colloid, which demonstrated that seventy percent of the nanostructures were nanostars. They concluded that other thirty percent of particles were formless groups of decahedra and rhomboids and that absorbance pinnacle of nanostars was identified to be in close infrared (840 nm). Hence, they believed that the gold nanostars developed were appropriate for biomedical applications, especially for photo-thermal therapy. For synthetic and organic sensor applications, plasmonic metal nanoparticles have extraordinary potential on grounds that to their touchy unearthly reaction to the nearby condition of nanoparticle surface and simplicity of checking the light flag because of their solid scrambling or retention. The affectability of plasmon reaction to size, shape and metal organization of gold and silver nanoparticles in detecting and imaging was accounted for by Lee and El-Sayed [26]. They researched the reliance of affectability of surface plasmon reverberation (recurrence and transfer speed) reaction to variations in their encompassing condition and general commitment of visual diffusing to aggregate eradication, on the size and state of nanorods and the kind of metal, that is, Au versus Ag. They saw that hypothetical thought at first glance plasmon reverberation condition uncovered that the ghostly affectability, characterized as relative move in reverberation wavelength as for the refractive file amendment of encompassing materials, has two governing elements, viz: right off the bat, mass plasma wavelength, a property subject to metal kind and

second on angle proportion of nanorods which is a geometrical parameter. They discovered that the affectability is straight relative to both these elements and that with the end goal to quantitatively look at reliance of ghostly affectability on nanorod metal organization and perspective proportion, the isolated dipole guess strategy was utilized for computation of photosensitive spectra of Ag-Au alloy metal nanorods as a function of Ag concentration. They additionally have seen that affectability does not rely upon the kind of metal but rather relies generally on viewpoint proportion of nanorods and that immediate reliance of affectability on perspective proportion turns out to be fairly more prominent as extent of nanorods ends up bigger. They notwithstanding reasoned that utilization of bigger nanoparticles may actuate an over the top expanding of reverberation range because of an expansion in the commitment of multipolar excitations, which can confine the detecting goals and they ascribed this coldheartedness of the plasmon reaction to the metal piece to the way that the mass plasma recurrence of the metal, which decides the unearthly scattering of the genuine dielectric capacity of metals and surface plasmon reverberation condition, has a comparative incentive for honorable metals. Notwithstanding, nanorods with higher Ag focus demonstrate an extraordinary upgrade in greatness and sharpness of plasmon reverberation band, which gives better detecting goals in spite of comparative plasmon reaction and that Ag nanorods have an extra favorable position as better scatterers contrasted and Au nanorods of a similar size.

For applications in biochemical detecting and organic imaging, noble metal nanoparticles have extraordinary ability in view of their one of a kind photosensitive properties deriving from the excitation of nearby surface plasmon resonances. Chen et al. [3] studied gold nanoparticles with restrained size, shape and passivating agents, alongside another procedure of guided self-assembly to make two-dimensional nanostructures from such nanoparticles.

Based on their optical properties, the determination of nanoparticles for accomplishing proficient differentiation for natural, cell imaging applications and for photothermal remedial applications is extremely urgent. Jain et al. [20] utilized the Mie hypothesis and discrete dipole estimation technique to compute ingestion and scrambling competences and photosensitive reverberation wavelengths for three normally utilized classes of nanoparticles, viz: gold nanospheres, silica-gold nanoshells and gold nanorods. They concluded that the determined spectra unmistakably mirrored the outstanding reliance of nanoparticle optical properties, viz: the reverberation wavelength, the annihilation cross-area and the proportion of dissipating to retention, on the nanoparticle measurements and that by expanding the extent of gold nanospheres from 20 to 80 nm, the size of elimination and the general commitment of scrambling to the termination quickly expanded and that gold nanospheres in the size range ordinarily utilized (~40 nm) demonstrated an assimilation cross-segment of ~5 orders greater than traditional retaining colors, while the greatness of light diffusing by 80-nm gold nanospheres was 5 orders higher than the light emanation from firmly fluorescing colors. They likewise have seen that the variety in plasmon wavelength most extreme of nanospheres, i.e., from 520 to 550 nm, was nonetheless too restricted to be in any way valuable for in vivo applications and that gold nanoshells were found to have optical cross-areas when contrasted with (and much higher than) nanospheres. Furthermore, they inferred that their optical resonances lied

positively well in close infrared district and that the reverberation wavelength can be quickly expanded by either expanding the aggregate nanoshell measure or expanding the proportion of the center to-shell sweep. They likewise deduced that the aggregate annihilation of nanoshells demonstrates a straight reliance on their aggregate size, nonetheless, it is free of the center/shell range proportion and that the relative scrambling commitment to the eradication can be quickly expanded by expanding the nanoshell measure or diminishing the proportion of the center/shell span. They likewise reasoned that gold nanorods demonstrated optical cross-segments, which were tantamount to nanospheres and nanoshells, be that as it may, at generally littler successful size. They additionally have seen that their optical reverberation can be directly tuned over the close infrared locale by changing either the successful size or perspective proportion of nanorods, while the aggregate annihilation and relative dispersing commitment expanded quickly with viable size, in any case, they were free of the angle proportion. With the end goal to think about viability of nanoparticles of various sizes for genuine biomedical applications, they determined the size-standardized optical cross-segments or per micron coefficients and presumed that gold nanorods indicated per micron ingestion and dissipating coefficients that are a request of greatness higher than those for nanoshells and nanospheres. Their decision showed that while nanorods with a higher viewpoint proportion alongside a littler viable span were the best photograph retaining nanoparticles, the most astounding diffusing complexity for imaging applications was gotten from nanorods of higher aspect ratio with a bigger viable radius.

Choi et al. [4] examined the affectability improvement in chemical sensors by coupling Au nanoparticles that have explicit size and surface density on sensor chips as those found in label-free identification frameworks. They conjugated Au particles with 10, 30 and 60 nm distance across by amine gatherings of cystamine-changed chips and controlled the surface density of Au by response time and convergence of arrangement containing the particles. In order to examine the sensitivity enhancement, they compared the resonance angle shifts with or without particles of Au in aqueous solution of methanol and observed that the sensitivity is a function of the surface density and size of the particles and they concluded that the sensitivity increased by 57% with adsorption of 30 nm particles' diameter and low surface density, which is a result of the coupling effect of localized surface plasmon obtained by size and density of specific Au nanoparticles and surface plasmon waves.

A green synthesis technique involving the use of an aqueous extract of garlic, i.e., *Allium sativum* L. (ASL) as a stabilizing and reducing agent was employed for successful production of gold nanoparticles (AuNPs) [51]. The active compounds in aqueous ASL were identified by authors and were extracted by a process of phytochemical analysis and FTIR spectroscopy, while the characterization of synthesized AuNPs was done using UV-Vis spectrophotometer and TEM-SAED. They concluded that there was formation of AuNPs, following the optimization of the ASL extract at a concentration of 0.05%, $HAuCl_4$ pH of 3.6 and concentration of 2.0×10^{-4} M. Optimized AuNPs was characterized with the aid of TEM and recorded a spherical shape with 15 ± 3 nm as the particle size, with particles remaining stable for up to one month duration and they concluded that the study of interaction of AuNPs synthesized with melamine and showed 3.6 as the optimum pH of interaction.

The green gold nanoparticles' synthesis by using extracts from plant as a reducing agent was reported by Elia et al. [11]. They prepared the gold nanoparticles (AuNPs) by using four different plant extracts, from the plants, viz: (a) *Salvia officinalis*, (b) *Lippia citriodora*, (c) *Pelargonium graveolens* and (d) *Punica granatum*, as reducing and stabilizing agents. They determined the size distributions of the AuNPs by using three different methods, viz: (i) dynamic light scattering, (ii) nanoparticle-tracking analysis and (iii) analysis of scanning electron microscopy images and concluded that similar size distributions were observed when three methods where utilized. Biocompatibility test was done by L-cell growth correlation in the presence of various amounts of AuPs and concluded that all the AuNPs showed improved stability and biocompatibility for more than 3 weeks, hence the author concluded that it can find useful application for drug delivery and imaging in human body. The shapes of AuNPs were observed with high-resolution transmission electron microscopy, while IR spectroscopy was used to characterize the different functional groups in organic layer which stabilizes the particles. They, therefore, concluded and proposed the active ingredients in plant extracts that may have been involved for AuNPs formation, based on the experiments with pure antioxidants which exist in that plant.

1.2.1 Silver, Gold and Bimetallic Nanoparticles Production

Govindaraju et al. [18] reported on the production of bimetallic nanoparticles via the interaction of a single-cell protein of *Spirulina platensis* with aqueous $HAuCl_4$ and $AgNO_3$. The author investigated synthesis nanoparticles such as: Au, Ag and Au core-Ag shell. The synthesis was carried through a biological reduction and extracellular synthesis of nanoparticles was achieved over a 120 h at 37 °C and pH of 5.6. They characterized the nanometallic dispersions by surface plasmon absorbance by measuring at 530 and 424 nm respectively for Au and Ag nanoparticles and concluded that for bimetallic nanoparticles, the observed absorption peaks were respectively at 509, 486 and 464 nm at 25:75, 50:50 and 75:25 (Ag:Au) mol concentrations,. They concluded that nanoparticle formation in range of 6–10 (gold), 7–16 (silver) and 17–25 nm (bimetallic 50:50 ratio) was observed by HRTEM and analysis using XRD of the gold and silver-validated formation of metallic gold and silver, while FTIR spectroscopic measurements showed that the possible biomolecule that is responsible for capping and reduction in biosynthesized nanoparticles is protein.

2 Green Polymer Composites and Nanocomposites Production and Their Applications

The use of synthetic composites has several disadvantages, hence the advent of green composite polymers. The main disadvantages, such as: non-biodegradability and disposal problem are real and these drawbacks are growing, hence the need and the stringent efforts of having alternatives by using natural fiber reinforced polymers, are crucially important. Most often, green composites consist of biodegradable natural reinforcement and a polymer matrix. Biocomposites find applications, mainly

in the construction and automotive industries. Globally, the development of green composites is ongoing to improve the applicability and efficiency of these materials. The reuse of agricultural wastes encouraged the strong efforts in the development of green composites.

When the sizes of materials, of which cellulose is no exception, are decreased down to nanoscale, unanticipated and very attractive properties can be achieved, of which cellulose is no exception. This is especially so with cellulose of highly reactive surface, emanating from the hydroxyl groups high density, which is exacerbated at this scale.

Liu et al. [28] fabricated Cefepime (CFP)-loaded polymer O-carboxymethyl chitosan (OCMC) microspheres (CFP-OCMC-MPs). It is noteworthy to know that Cefepime (CFP) is most frequently utilized antibiotic for post-surgery infection prevention, since the systemic delivery of CFP in a bulk dose mostly shows an efficient therapeutic effect, while cytotoxicity can equally be generated. This drawback in the use of this antibiotic can be minimized by local and controlled drug administration to prolong therapeutic effects and reduce cytotoxicity by sustaining drug release and minimizing drug exposure. Liu et al. [28] synthesized CFP-loaded polymer *O*-carboxymethyl chitosan (OCMC) microspheres (CFP-OCMC-MPs) and its antimicrobial activity against *Staphylococcus aureus* and its biocompatibility was evaluated. They concluded that microspheres possessed the spherical surface with diameter of ~7 μm and that Fourier transforms infrared spectral and wide-angle XRD analysis showed that CFP was steadily incorporated. Also, they inferred that the drug loading content and the protective sheet efficiency of the microspheres were 21.4 ± 0.5% and 42.3 ± 0.7%, respectively. In addition, the drug release profiles were found to be biphasic with an initial burst release followed by a gradual release phase, following the Higuchi model and that CFP-OCMC-MPs were capable of killing all the bacteria cultured in suspension within 24 h and exhibited long-lasting bactericidal activity as demonstrated by inhibition zone study. They further inferred that when compared to CFP, CFP-OCMC-MPs showed a milder toxicity toward *osteoblast*-like cells over an 8 day period and that these results suggested that CFP-OCMC-MPs are endowed with the sustained treatment of bacterial infection and enhanced biocompatibility. A series of copolymer hydrogels were produced by Hu et al. [19] from poly(ethylene glycol) diacrylate (PEGDA) and methacrylated poly(γ-glutamic acid) (mPGA). They studied, in detail, the effect of pH and ionic strength on the mechanical properties and swelling behavior of these hydrogels. They also evaluated the emancipation of Rhodamine B as a model drug from hydrogel under varied pH. They performed in vitro photoencapsulation of bovine cartilage chondrocytes in order to evaluate the cytotoxicity of this copolymer hydrogel and concluded. The results revealed that the copolymer hydrogel is pH- and ionic-sensitive and did not exhibit acute cytotoxicity. There is a promising application for copolymer hydrogel as matrix for controlled and improved drug release and scaffolding materials in tissue engineering.

The combination of good thermal and mechanical properties with biodegradation ability is exemplified by aliphatic-aromatic copolyester, poly(butylene adipate-*co*-terephthalate) (PBAT), even though its potential medical applications were not realized until recently, since few research work of blends of PBAT with commonly

used biocompatible polymers had been prepared and investigated for applications in tissue engineering. Arslan et al. [2] reported on processing, structural characteristics and cellular responses of poly(butylene adipate-*co*-terephthalate) scaffolds. They determined neat PBAT processability as potential scaffold materials for applications in bone tissue by using various production techniques such as electrospinning, solvent evaporation, melt molding-particulate leaching and solvent casting-particulate leaching (SCPL). They concluded that data from physicochemical characterizations and cell culture studies with MC3T3-E1 preosteoblasts established that neat PBAT had promising characteristics for bone tissue engineering, even though production technique strongly influences the cellular responses. They, therefore, proposed from the data emanating from characterizations and cell cultures that PBAT scaffolds produced by electrospinning and SCPL are recommended to be used when it comes to bone tissue engineering.

With the fabrication of carbon nanomaterials, graphitic nanocapsules are becoming nanomaterials that are enjoying some degree of popularity because of their distinctive chemical and physical properties, as well as suitable biocompatibility, make them appropriate agents for biomedical and bioanalytical applications. If reasonable design is employed, impregnating graphitic nanocapsules with other materials can provide them with additional properties which will make them useful nanoplatforms for bioanalysis. Senthil et al. [44] prepared all cellulose green composites with cellulose as matrix and 5 wt% to 25 wt% Napier grass short fibers (NGSFs) as fillers. They characterized the matrix, filler and the green composites with randomly oriented NGSFs with XRD, FTIR spectroscopy, thermogravimetric analysis (TGA), polarized optical microscopy (POM) and tensile tests. They concluded that FTIR spectra indicated the presence of minute amounts of hemicelluloses and lignin in filler and composites. The crystallinity of composites was found to be lesser than that of cellulose. They also found out that the thermal properties of composites were greater than that of the matrix and such properties improved with filler content, while the tensile strength of composites, although was lesser than that of the matrix, was still greater than that of thermoplastics (high-density polyethylene and polypropylene) and that the cellulose/NGSFs composites can suitably be considered for biodegradable packaging applications.

Cellulose, being the most abundant and important plant natural polymer, has a number of fascinating properties including those that make it attractive as biodegradable natural filler in matrix of thermoplastic polymer composite materials. In a relatively short period (i.e., between 2007–2012) and with regards to conforming with the standards of green technology, the production of such composite materials increased from 0.36 to 2.33 million tons and it is forecast that by the year 2020, the production of such composites will increase to 3.45 million tons [35]. Paukszta and Borysiak, on the ground of currently published literature, which illustrate the many aspects of the difficulties related to the prospect of using lignocellulosic components for the fabrication of polymeric composites, reviewed that the lignocellulosic materials presently in use as polymer fillers, by considering the factors that determine the macroscopic properties of such composites with specific attention to poor interfacial adhesion between lignocellulosic filler and polymer matrix and to cellulose occurrence effects

in polymorphic varieties. Considering the controlling nucleation potentials of lignocellulosic filler, a typical phenomenon of cellulose polymorphism, the composites mechanical properties, can be considerably improved and this can be of significant importance. In addition, green composite macroscopic properties depend on the processing parameters, which will consequently determine the significance and extent of shearing forces, just as effect of shearing forces appears on the processing of polymer matrix final supermolecular structure. From the ecology viewpoint, the likelihood of composite recycling which should most likely be taken into account at design stage is highly important. Hence, the methods of recycling composites that are made of thermoplastic polymers, filled with renewable lignocellulosic materials, are similarly important and at the same time, taking these recycling methods into consideration, at the initial design stage.

Scarica et al. [42] reported on lignin functionalization with succinic anhydride as a building block for bio-based thermosetting polyester coatings. The materials were based on the soluble fraction functionalization of softwood kraft lignin recovered from solvent extraction with growing amounts of succinic anhydride (SAn), to obtain SAn/lignin adducts through the formation of ester bonds on lignin hydroxyl. They carried out very comprehensive physical, chemical and thermal characterizations of resulting materials that were esterified in order to confirm effective covalent inclusion of SAn in the lignin macromolecule. They employed the functionalized SAn/lignin adducts as building blocks for production of cross-linked lignin-based polyethylene (PE) coatings under varying curing conditions. They concluded that the PE coatings showed enhanced thermal stability, solvent resistance, film-forming ability, higher hydrophobic character and dynamic surface hardness in comparison with the parent lignin precursor that was not modified. They also assessed the adhesion strength/nature of these systems on different substrates and that the results demonstrated a simple accessible method to produce high lignin content thermosetting polyethylene systems and provided indication of the ability of these materials as bio-derived adhesives and coatings.

Even though chemical graft polymerization modification is one of the facile strategies for promoting the industrial uses of lignin, the selection of a highly efficient initiation system, still remains a formidable challenge. Zong et al. [54] attempted to comprehend $CaCl_2$–H_2O_2 system in introducing the graft polymerization of acrylic monomers onto acetic acid lignin (AAL) and biobutanol lignin (BBL). They found out that the initiation system was highly selective and efficient, as exemplified by successful graft of polyacrylates onto lignin and they also proposed possible mechanism. They concluded that the thermal characterization of materials showed that graft modification resulted in Tg and higher thermal stability of lignin and that graft modification made AAL and BBL to develop highly hydrophobic than it was before it was modified and that by inclusion, a small quantity of lignin-graft-polyacrylate can substantially improve the ultra-violet (UV) blocking capability coupled with reinforcing impact on PLA, hence presenting a highly effective, novel and selective free radical initiation system for functionalization of lignin. Eisa et al. [8], successfully synthesized silver nanoparticles held within polyvinyl alcohol (PVA)/polyvinylpyrrolidone (PVP) films, by employing a novel in situ technique, with PVA and PVP, respec-

tively, acting as polyol reductant and stabilizer. They successfully incorporated Ag nanoparticles into PVA/PVP matrix, which was established by UV-Vis, TEM, XRD and FTIR spectroscopy. They concluded that the PVA/PVP-stabilized Ag nanocomposite film showed presence of properly distributed and spherical Ag nanoparticles have an approximately 30 nm average diameter, while the percentage increase in PVP resulted in a reduction in the particle sizes.

With varied shapes and sizes, diverse surface chemistry, biology and the porous nature of it cell walls, microbes are a significant part of life. This is in addition to their significance in industrial practices e.g., in fermentation process. These function as biotemplates by providing a biomimetic method for the production of multifarious complex constructs, with pre-defined structures, such as: ordered hybrid nanomaterials and composites micro/nanorobots and microdevices through different approaches [45]. The building blocks for such strategies can be: algal, bacterial, and virus particles or fungal cells. Shi et al. summarized the recent advances in biofabrication based on live microbes. They concluded that by employing engineering methods and employing appropriate techniques, live microbes can, at will, be influenced as functional "micro/nanodevices and robots" to further carry out biological functions, like distribution, replication, motility, secretion of metabolites and formation of colonies; and that biofabrication based on microbes can provide effective techniques to control and manipulate the microbes as a functional live building blocks to produce micro/nano devices and robots for applications in biomedical and energy.

Wang et al. [50] designed and prepared the well-known magnetic recyclable bactericidal nanocomposites (Fe_3O_4@PDMC) by coating of Fe_3O_4 nanoparticles with quaternarized *N*-halamine polymers via a free radical polymerization process, in which 5,5-dimethylhydantoinyl-(3-ethyl-methacrylamide)propyl dimethylammonium bromide (DEMPA), a new monomeric *N*-halamine precursor, was used as a coating material and as a dual-functional bactericidal agent. They observed that the Fe_3O_4@PDMC nanocomposites developed, exhibited suitable size and super-paramagnetic responsibility, while the antibacterial results showed that the Fe_3O_4@PDMC nanocomposites had excellent biocidal abilities against *E. coli* (gram-negative) and *S. aureus* (gram-positive). They further observed that the TTC (Triphenyl Tetrazolium Chloride)-dehydrogenase activity assay confirmed that the reductions of bacteria were mainly attributed to powerful biocidal effects of coating polymer, instead of bacteria capture by cationic surface. They concluded that as a result of the magnetic responsive performance of Fe_3O_4, the as-prepared Fe_3O_4@PDMC nanocomposites are recyclable by a magnet and can be reused for anti-bacterium through the quenching/re-chlorination procedure. They are of the belief that the proposed Fe_3O_4@PDMC nanocomposites can be a competitive candidate for water purification systems and household sanitation. Salama et al. [40] reported on the synthesis, characterization and biological activity of cross-linked chitosan biguanide loaded with Ag nanoparticles. They characterized the synthesized chitosan biguanide hydrochloride (ChG) and glutaraldehyde cross-linked chitosan biguanide (CChG) by FTIR spectroscopy, ^{1}H NMR and ^{13}C NMR, XRD, thermal analyses (TGA and DTA) and scanning electron microscopy (SEM). They concluded that results of study showed that ChG and CChG had a more amorphous structure

than chitosan and their thermal stability was slightly lower than that of chitosan. They prepared also colloidal silver nanoparticles (AgNPs) by using borohydride reduction method and then investigated the AgNPs as fillers in partially cross-linked chitosan biguanide. They concluded that nanoparticles obtained were of uniform and spherical with 9.6 ± 0.5 nm as average size, while CChG/AgNPs composites prepared were characterized for their morphology, thermal properties, cytotoxicity and antimicrobial activity. They concluded that SEM images revealed that AgNPs are well incorporated in the CChG matrix and CChG thermal stability was improved with the inclusion of AgNPs. They further concluded that CChG and CChG/AgNPs showed less cytotoxicity to breast cancer cells (MCF-7) and that when compared with chitosan and CChG, ChG and CChG/AgNPs showed better antimicrobial activity against *Geotrichum candidum* and *Syncephalastrum racemosum* as fungi.

Juturu and Wu [23] discussed the production of microbial of lactic acid with emphasis on the latest development. In production of polylactic acid (PLA), lactic acid is a valuable platform chemical and other important added products and it is naturally developed by a wide spectrum of microbes which including yeast, filamentous fungi and bacteria. Bacteria fermentation of C5 and C6 sugars to produce lactic acid is either by homo- or hetero-fermentative mode. Among the important enzymes that influence the ways of producing lactic acid are transaldolase, phosphoketolase, xylose isomerase, ℓ- and *d*-lactate dehydrogenases. ℓ-lactic acid is produced from lignocellulose sugars homo-fermentatively under non-sterilized conditions by thermophilic *Bacillus coagulans* strains; however, the lack of genetic tools for metabolically engineering them has strictly affected their development for applications in the industries. In order to obtain fermentable sugars, pre-treatment of agriculture biomass is a prerequisite for the use of the huge amounts of biomass gotten from agricultural for the production of lactic acid; however, the main challenge is the availability of high concentrations of quality sugars in a way that is cost effective.

Therefore, in order to minimize or avoid completely the use of neutralizing agents during the process of fermentation, genetically engineering the strains to enable them oppose acidic environment and produce low pH lactic acid can be useful for reducing lactic acid production cost. Eiteman and Ramalingam [9] reported on the microbial production of lactic acid, since microbial production can efficiently compete with chemical synthesis approaches reason that biochemical synthesis allows the production of either one of the enantiomers having high optical purity at titer and high yield, a result which is specifically beneficial for the development of PLA polymers with specific/desired properties. This is because the availability of microbial lactic acid production in commercial quantity relies on the use of low-cost carbon substrates originating from waste or agricultural resources; hence, optimal lactic acid formation demands an understanding of the competing paths involved for carbohydrate metabolism, just as the paths leading to possible by-products are very crucial, of which both affect product yield. In their review work, Eiteman and Ramalingam discussed the latest research influences of these biochemical pathways, while researchers also continue to seek strains with enhanced tolerance and their ability to function under desired industrial conditions; for instance, in conditions at different temperatures and pHs.

3 Bio-Synthesized Nanomaterials for Drug Delivery Applications

When attaining the planned infected site in the human body, the drug carried by a substrate needs to be released if solid NPs are used for drug targeting. Therefore, biodegradable nanoparticle drug delivery formulations are essential since it is the aim to convey and deliver the drug so that it will be effective. Drug nanoparticle entrapment is either for improved delivery to, or uptake by, target cells or/and a decrease in toxicity of free drug to non-target organs, since the situations can lead to an increase in the therapeutic index, the margin between the doses leading to a therapeutic ability and toxicity to the other organ systems. The therapeutic ability can be tumor cell death.

The design of better approaches to treat various diseases that affect humans is of significant and this has led to the development and use of different materials of natural and synthetic origins as drug delivery devices, but not without some certain limitations and challenges have been faced with the use of most of these materials, therefore, the need for more suitable and feasible alternatives. Ordinarily, the primary aim for research of nano-bio-technologies in drug delivery includes but not limited to:

(i) Quicker development of novel, improved and safe medicines,
(ii) Improved specific drug targeting and delivery,
(iii) Greater safety and biocompatibility,
(iv) Decrease in toxicity while the therapeutic effects are maintained.

Liu et al. [29] reported on the preparing alginate hydrogels through process known as solution extrusion and the different drugs release behavior. They fabricated homogeneous alginate hydrogels through the process of solution extrusion, where D-glucono-δ-lactone (GDL) and $CaCO_3$ were utilized as the gelation agents. They further reported that slow gelation of alginate was achieved by in situ release of Ca^{2+} from $CaCO_3$ particles which is induced by hydrolysis of GDL to reduce pH and that little gelation during extrusion caused enhanced strength of the alginate solutions, leading to the extrudability of blends. They concluded that this method enabled production of alginate hydrogels in a single step via extrusion, which was more economically advantageous to the conventional laboratory-scale preparation for mass production. They employed three different drugs, viz: ibuprofen, acetaminophen and methylthionine chloride, as model drugs in order to evaluate drug release behavior of the alginate hydrogels. They concluded that it was demonstrated that the drug release behavior was significantly adjusted by the drug solubility and the ionic interaction between alginate and the drug molecule. Also, it was concluded that the process showed that solution extrusion process is a feasible method to produce alginate-based drug delivery systems.

Zhang et al. [52] developed novel glutathione (GSH)-dependent micelles, based on carboxymethyl chitosan (CMCS) for the triggered intracellular release of doxorubicin (DOX). DOX-33′-Dithiobis (N-hydroxysuccinimidyl propionate)-CMCS

(DOX-DSP-CMCS) prodrugs were synthesized and DOX was attached to the amino group on CMCS via disulfide bonds and drug-loaded micelles were formed by self-assembly. They concluded that the micelles formed a core-shell structure with CMCS and DOX as the shell and core, respectively, in aqueous media. They confirmed the structure of the prodrugs by IR and 1H NMR spectra and concluded that drug loading capacity as determined by UV spectrophotometry was 4.96% and the critical micelle concentration of polymer prodrugs determined by pyrene fluorescence was 0.089 mg/mL. In addition, they concluded that the mMicelles were spherical and the mean size of the nanoparticles was ~174 nm, having a narrow polydispersity index of ~0.106; they also concluded that in-vitro drug release experiments showed that micelles were highly GSH-sensitive, as a result of the reductively degradable disulfide bonds. It was also concluded that cell counting kit (CCK-8) assays revealed that DOX-DSP-CMCS micelles exhibited effective cytotoxicity against *HeLa* cells and that confocal laser scanning microscopy (CLSM) demonstrated that DOX-DSP-CMCS micelles could efficiently deliver and release DOX in the cancer cells, while the DOX-DSP-CMCS nanosystem displayed a promising drug delivery vehicle for cancer therapy.

4 Bio-Mediated Synthesis of Nanomaterials for Antibacterial and Antimicrobial Applications

Metal nanoparticles synthesis via plant-mediated process is fast gaining recognition since it has the potentials of defeating the traditional synthesis methods like chemical and physical methods. Hence, a dependable and eco-accommodating procedure to produce metal nanoparticles is an essential phase in nanotechnology [38]. As reducing and stabilizing agents for the production of AgNPs, biomolecules, like: enzymes, amino acids, proteins, terpenoids and flavonoids from various plant extracts, have been utilized. In spite of the wide series of biomolecules, needed in the assistance in the production methodology, scientists face large challenges in the attempt to produce steady and geometrically controlled AgNPs. In this effort, several attempts have been prepared to develop plant-mediated synthesis in order to manufacture: cheap, stable and biodegradable AgNPs. Therefore, several hundreds of diverse plants extract sources for the production AgNPs have been illustrated in the last ten years by numerous scientists. Several criticisms had focussed on the diverse plant sources, synthetic techniques and characterization techniques for the distinguishing evaluation and antibacterial activity against bacterial of these products. Several surveys and works are in the general population space on the plant-mediated synthesis of AgNPs just as the antibacterial activity of AgNPs yet this particular article mainly centered around biomolecules of plants and its different parts and working conditions engaged in the production. Rajeshkumar and Bharath [38], succinctly reviewed the characterization of AgNPs and their antibacterial action by considering the size, shape, and strategy utilized for investigation.

Fig. 1 Photograph of *Emblica officinalis* plant [13]

Methods for the synthesis of nanoparticles, like chemicals and high physical energy procedures, can be toxic, especially if they are to be used in the biological and medicine fields. In order to overcome such negative consequences, the biological approach has been utilized for the synthesis of different metal nanoparticles. As mentioned, silver nanoparticles (AgNPs) have received considerable attention in different fields, like: therapeutics, antimicrobial activity, silver nanocoated medical devices, optical receptor and bio-molecular detection [49]. In their review work, Velusamy et al. [49] reported on the bio-inspired green nanoparticles: synthesis, mechanism of synthesis and their antibacterial applications, especially in the biomedical fields. They concluded their report by inferring that biological approach, in particular, usage of natural organisms has presented a reliable, nontoxic and environmentally friendly technique. On the other hand, Ramesh et al. [39] reported on the straight forward green synthesis of silver nanoparticles (AgNPs) in an aqueous medium designed to use *Emblica officinalis* (*EO*) fruit extract as a reducer and stabilizer. They discovered that formation of AgNPs depends on the effect of extract concentration and pH and that the AgNPs can be synthesized by using *E. officinalis* (fruit extract). The resultant nanoparticles were characterized by UV-Vis spectrophotometer, while the occurrence of biomolecules of *E. officinalis*, capped in AgNPs was confirmed by FTIR and the size and shape were studied with XRD and SEM confirmed the crystalline nature of silver nanoparticles; the mean size of AgNPs as determined by the XRD, was found to be around 15 nm. They employed the AFM to determine and verify the morphological features. They concluded that shape of biosynthesized AgNPs is spherical. They succeeded in capping *E. officinalis*, like polyphenols, glucose and fructose with AgNPs, reduced toxicity. They are of belief that *E. officinalis* fruit extract is a promising bioreductant for AgNPs, which exhibit reserve and had a substantial antibacterial action against both gram-positive and gram-negative bacteria. Figure 1 shows the photograph of *E. officinalis*.

Fig. 2 Photograph of *Sesuvium portulacastrum* L. plant [15]

Biomedical applications of Ag nanoparticles are among the very many fields of Ag°s. This is a result of their outstanding antibacterial properties. Raja et al. [37] discussed the use of extract of fresh leaves of *Prosopis juliflora* for synthesis of silver (Ag°) and employed UV-Vis studies for the study of the formation of Ag° within 5 min, while SEM was used to describe shape of Ag nanoparticles, XRD confirmed nanoparticles as crystalline silver with a face-centered cubic crystal form and FTIR showed biomolecule compounds that were responsible for capping and reduction material of Ag nanoparticles. They performed antimicrobial activity of nanoparticle by sewage and concluded that method of plant-mediated can be cost effective, eco-friendly and relatively relaxed method for the production of Ag°, when compared to the chemical and physical methods. On the other hand, Nabikhan et al. [31] reported on the synthesis of antimicrobial silver nanoparticles by using callus and leaf extracts from saltmarsh plant, *Sesuvium portulacastrum* L. They suggested that the callus extract was able to develop silver nanoparticles, better than leaf extract and the synthesis of silver nanoparticles was confirmed with X-ray diffractogram, which exhibited intense peaks that corresponded to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) sets of lattice planes of silver. Generally, the Ag nanoparticles manufactured are found to be spherical in shape with a constant change in the size ranging between 5 and 20 nm, as observed with transmission electron micrographs. FTIR spectroscopy measurement revealed prominent peaks in the extracts corresponding to amide I, II and III, thereby indicating occurrence of protein. These peaks are in addition to those that corresponded to: aromatic rings, geminal methyls and ether linkages, which indicated presence of flavones and terpenoids that are responsible for the stabilization of Ag nanoparticles. They concluded that the silver nanoparticles were seen to have inhibited clinical strains of bacteria and fungi and that antibacterial activity was extra unique than antifungal activity. Figure 2 shows the photograph of *Sesuvium portulacastrum* L. plant.

Fig. 3 Photograph of *Tribulus terrestris* L. plant [16]

The modification of Fe_3O_4-functionalized nanoparticles with *N*-Halamine and the study of their magnetic/antibacterial properties were carried out by Dong et al. [7]. They fabricated magnetic/antibacterial bifunctional nanoparticles via the immobilization of antibacterial N-halamine on silica-coated Fe_3O_4-decorated poly(styrene-*co*-acrylate acid) (PSA) nanoparticles. They characterized the samples by using SEM, TEM, X-ray diffraction (XRD), (EDX), FTIR, energy-dispersive X-ray spectrometry, X-ray photoelectron spectra (XPS) and thermogravimetric analysis (TGA). They concluded that the N-halamine was developed from the precursor 5,5-dimethylhydantoin (DMH) by chlorination treatment and that the experimental data showed that the loading amount of DMH on the silica-coated Fe_3O_4-decorated poly(styrene-*co*-acrylate acid) nanoparticles was adjustable.

As a result of their outstanding and ever-increasing applications, the increased development of the green synthesis of nanoparticles seems to be inevitable and not unexpected. As a consequence, there are huge volumes of works that have been reported, based on plant and its extract-mediated synthesis of nanoparticles. Gopinath et al. [17] explored the novel techniques for biosynthesis of Ag nanoparticles by utilizing fruit bodies of plants. Figure 3 shows the photograph of *Tribulus terrestris*. They used plant, *Tribulus terrestris* L. fruit bodies in their research, where extracted dried fruit body was mixed with silver nitrate in a bid to synthesis of Ag nanoparticles. They reported the active phytochemicals present in plant were main reason for rapid reduction of silver ion (Ag +) to metallic silver nanoparticles (Ag°).

Following reduction process, silver nanoparticles produced were characterized by TEM, XRD, AFM, FTIR and UV-vis spectroscopy. They observed spherically-shaped silver nanoparticles with sizes ranging between 16–28 nm, while diffraction pattern equally established that greater percentage of Ag with fine particles sizes. They determined the antibacterial property of nanoparticles. They concluded that plant materials-mediated synthesis of silver nanoparticles has comparatively rapid and cost effective, efficient and can have a wide range of applications, especially in antibacterial therapy, needed in modern medicine.

5 Medical and BioMedical Applications of Bio-Mediated Nanomaterials

Advancement in treatment of restenosis has been very significant as a result of use of drug-eluting stents (DES) since they have considerably lessened the necessity of repeat revascularization processes and with outstanding results recorded in various patient subsets, these devices are now used in many stent implantation procedures. With the expanding number of patients getting drug-eluting stents and accessibility of long-term follow-up information, concern has been raised with well-being of these gadgets. The concern has potential for expanded inflammatory and thrombogenic reactions and their perilous outcomes related with polymers utilized for delivery of anti-restenotic agents are of incredible concern. The concern has the potential for expanded inflammatory and thrombogenic reactions and their perilous outcomes are related to the polymers utilized for delivery of anti-restenotic agents are of incredible concern. Usually, a stent is a small mesh tube employed to treat narrow or anemic arteries. The red-blockage of coronary artery remains one of drawbacks of percutaneous coronary mediations even in age of drug-eluting stents (DES). The working rule of DESs, basically, comprises of delivery of controlled measures of antiproliferative agents at nearby dimension, which can result in concealment of neointimal expansion, fundamental driver of lumen re-narrowing after stent implantation. For present, a lot of DES platforms have been created and assessed for clinical use and they contrast between them with respect to the: stent type, hostile to proliferative medication, presence of polymers utilized for drug storage and modification of drug release kinetics as well as type of polymer utilized for this purpose. Despite the fact that their mid-term viability has been entrenched, there still remain, a continuous discussion on capability of an expanded rate of late stent thrombosis, especially after stoppage of thienopyridine treatment and of delayed beginning of restenosis or make up for lost time with DESs and on animal and human neurotic information, researchers have connected previously mentioned worries to presence of polymers in DESs, which have a pro-inflammatory and prothrombinogenic potential, and at times may incite an hypersensitivity reaction. Polymer-free stents with a microporous surface as an option in contrast to stents utilizing polymeric coating for local drug delivery have generated a lot of interest. This has brought about improvement of a portable framework which empowers coating in catheterization laboratory of polymeric free stents with various medication dosages or blends. With the utilization of a porcine coronary model of restenosis, empowers coating with rapamycin of a polymer-free microporous stent is possible and successfully lessens neointimal expansion. Non-polymer coating with rapamycin can be safe and leads to a dose-dependent reduction in restenosis.

It is exceptionally alluring to have malignant growth treatments that are less poisonous and intrusive than their current partners. Toward this path, evaluation of radiofrequency interaction with gold nanoparticles and biological systems for non-intrusive hyperthermia malignant growth treatment was made by Corr et al. [5]. Presently, the utilization of RF electric fields that enter deeply into the body,

causing insignificant harmfulness, is being examined as a reasonable method for non-intrusive malignant growth treatment. It is imagined that collaborations of RF energy with internalized nanoparticles (NPs) can liberate heat which would then be able to cause overheating (hyperthermia) of the cell, at last end in cell putrefaction. Researcher exhibited all around nitty gritty conventions identifying with evaluating the warmth freed by exceptionally focussed NP colloids for non-biological system, on account of in vitro analyses, they depicted the procedures and conditions, which must be clung to so as to adequately open malignancy cells to RF energy without bulk media heating artifacts by significantly obscuring the data, while concluding with a methodology for in vivo mouse models with ectopic hepatic cancer tumors. It is fundamental that correct delivery of cells to target organs is possible for the accomplishment of cell-based treatments with undifferentiated organisms or insusceptible cells, for example, antigen-showing dendritic cells (DC) while marking with different agents before implantation gives an incredible way for checking cell movement utilizing attractive reverberation imaging (MRI) [43]. Schwarz et al. [43] researched the take-up of completely orchestrated or bacterial attractive nanoparticles (MNPs) into hematopoietic Flt3+ undifferentiated organisms and DC from mouse bone marrow and reasoned that (i) take-up of both manufactured and biogenic nanoparticles into cells supply attractive action and (ii) low quantities of MNP-stacked cells, are promptly recognized by MRI.

For specific catalysts, nucleic acids and antibodies, bacterial magnetosomes (BMs) are regularly utilized as vehicles despite the fact that they are not frequently considered as medication carriers. So as to assess clinical capability of BMs separated from *Magnetospirillum gryphiswaldense* in malignancy treatment, doxorubicin (DOX) was stacked onto the filtered BMs at a proportion of 0.87 ± 0.08 mg/mg by utilizing glutaraldehyde [46], they discovered that the DBMs discharged DOX gradually into serum and kept up in any event 80% solidness, following a 48 h of hatching, while in vitro cytotoxic tests demonstrated that the DBMs were cytotoxic to HL60 and EMT-6 cells, showed as restraint of cell expansion and concealment in c-myc articulation, predictable with DOX. They presumed that these perceptions portrayed in vitro antitumor property of DBMs like DOX and methodology of coupling DOX to magnetosomes may have some amazing clinical potential in antitumor drug delivery. Figure 4 shows *M. gryphiswaldense* bacterium.

Fu et al. [12] reviewed the present status and utilization of bacterial cellulose also called microbial cellulose-based materials (which is a characteristic polymer which is biosynthesized by specific microscopic organisms) for skin tissue fixation. The work focussed on BC-based materials which can be used for skin tissue fixation, which has interesting basic and mechanical properties when put side by side with the higher plant cellulose and it is visualized to become a useful material. In their survey, they abridged the essential properties and distinctive sorts of BC, including self-assembled, oriented BC and various BC and investigated the composites arranged by utilizing BC related to different polymers and tended to the exploration on BC for application in skin tissue designing. They at long last analyzed some trial results and clinical medications by evaluating the execution of wound recuperating materials, in light of BC. They reasoned that with its prevalent mechanical properties and its

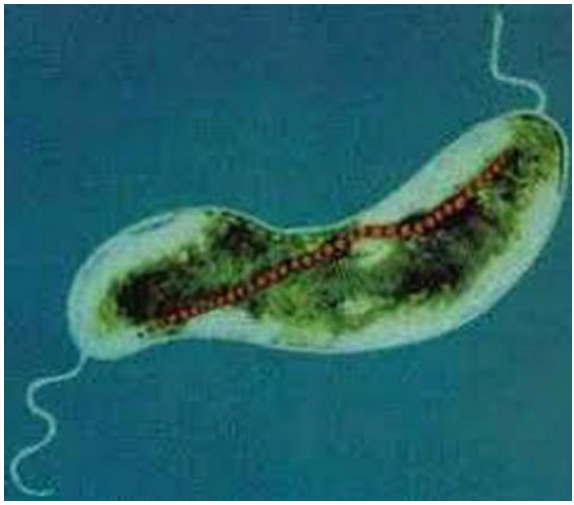

Fig. 4 Photograph of *Magnetospirillum gryphiswaldense* bacterium [14]

astounding biocompatibility, BC appeared to have incredible potential for biomedical application and extremely high clinical incentive for skin tissue fixation.

As an outcome of aggregation of uremic poisons in blood, this may instigate chronic renal failure (CRF), which can have an occurrence rate of ~10%. The customary treatment for CRF was hemodialysis, which was increasingly viable to expel little molecules, for example, urea and creatinine [53]. Zhou et al. utilized a twofold lyophilization technique for the production of CS/GO-COOH scaffold and concentrated its application in blood detoxification. Researchers built up another sort of chitosan/carboxyl graphite oxide (CS/GO-COOH) scaffold by means of a twofold lyophilization strategy. The scaffold was characterized by Fourier change infrared spectroscopy, checking electron magnifying lens, hydrophilic test, mechanical properties and in vitro detoxification test. They saw that covalent holding and hydrogen holding were shaped, demonstrating the solid communications among CS and GO-COOH and that there were some interconnected systems in the combined scaffold. They reasoned that the mechanical test recommended that the GO-2500 Scaffold had magnificent mechanical quality, which was 7.41 ± 0.82 MPa with 25% psychologist. Following pressure of up to 90% psychologist, they discovered that the GO-2500 could rebind absolutely, within a second. They observed the rates of GO-2500 water uptake and the retention data to be: 1587 ± 60 and 246 ± 10%, respectively and concluded that the CS/GO-COOH scaffold held enormous potential for the detoxification of uremic toxins.

The chemical stability assessment of trimethylsilane plasma nanocoatings for coronary stents was made by Jones and his colleagues [21]. They deposited by means of plasma nanocoating, Trimethylsilane (TMS) onto tempered steel coupons in direct current (DC) and radio recurrence (RF) gleam release with an extra NH_3/O_2 plasma treatment to tailor the covering surface properties. They assessed the synthetic strength of the nanocoatings following multi-week stockpiling under dry condition

(25 °C) and inundation in reproduced body liquid (SBF) at 37 °C. They reasoned that nanocoatings did not impact surface harshness of hidden treated steel substrates. They utilized X-beam photoelectron spectroscopy and FTIR spectroscopy to describe the surface science and creations and inferred that DC and RF nanocoatings had Si- and C-rich pieces and the O- and N-substance on the surfaces were generously expanded after NH_3/O_2 plasma treatment. Then again, they reasoned that contact edge estimations demonstrated that DC-TMS nanocoating with NH_3/O_2 treatment produced exceptionally hydrophilic surfaces, while DC-TMS nanocoatings with NH_3/O_2 treatment indicated insignificant surface science change following 12-week drenching in SBF. They further arrived at the resolution that nitrogen functionalities on RF-TMS covering with NH3/O2 post-treatment were not as steady as in DC case, while cell culture contemplates uncovered that surfaces with DC covering and NH_3/O_2 post-treatment exhibited significantly enhanced multiplication of endothelial cells over multi-week stockpiling period at dry and wet conditions when contrasted with other covered surfaces. At last, they presumed that DC nanocoatings with NH_3/O_2 post-treatment might be artificially steady for long-term properties, including time frame of realistic usability stockpiling and presentation to the circulatory system for coronary stent applications.

Teimouri et al. [47] incorporated β-chitin/nanodiopside/nanohydroxyapatite (CT/nDP/nHAp) composite scaffold from mix of chitin, nDP and nHAp in various inorganic/natural weight proportions by freeze drying method. They characterized composites by conducting: BET, TG, FTIR, SEM and XRD examinations. They inferred that composite scaffold had between 50 and 75% porosities with well-defined interconnected permeable systems. Moreover, they did an examination of the cell attachment and viability utilizing MTT, DMEM arrangement and mouse preosteoblast cell demonstrated the cytocompatible idea of composite scaffold with enhanced cell attachment and presumed that outcomes predominantly represented that composite can be a decent possibility for bone tissue designing application.

6 Bio-Mediated Synthesis of Nanomaterials for Anticancer Applications

The green synthetic routes of nanoparticles eradicate the necessity for a stabilizing and capping agent and they display shape and size-dependent biological activities. This is because natural plant concentrates encompass expansive varieties of metabolites that include: alkaloids, phenolic compounds, carbohydrates, terpenoids, and enzymes, among others. Patil and Kim [34] reviewed the biodegradable process for the production of silver nanoparticles (AgNP) and gold nanoparticles (AuNP) and focus on the mechanism of the antibacterial activity of AgNPs and the anticancer activity of AuNPs. In a one-step and eco-friendly process, biomolecules in the plant concentrates are involved in the reduction of metal ions to the nanoparticle. They described certain plant concentrates that are used in nanoparticle synthesis, character-

ization techniques and their biological applications. Such nanoparticles are essential in the field of pharmaceuticals as a result of their resilient antibacterial and anticancer activity and in particular, their significance and exceptionality of this concept of nanoparticles in general, the synthesis, characterization and application of AgNPs and AuNPs.

Multidrug-resistant bacterial infections are of great concern in the specialty of wound care. Li et al. [27] reported on bacterial cellulose (BC) adorned by 4,6-diamino-2-pyrimidinethiol (DAPT)-reformed gold nanoparticles (Au-DAPT NPs) presented as a dressing (BC-Au-DAPT nanocomposites) for the treatment of bacterially infected wounds. They concluded that BC-Au-DAPT nanocomposites had superior ability when estimated in terms of condensed minimum inhibition concentration than most of the antibiotics (cefazolin/sulfamethoxazole) alongside Gram-negative bacteria, while upholding exceptional physicochemical properties, which include: biocompatibility, water absorption ability and mechanical strain. In addition, their conclusions included the fact that on *E. coli*- or *Pseudomonas aeruginosa*-infected full-thickness skin wounds on rats, the BC-Au-DAPT nanocomposites inhibited bacterial growth and promoted wound restoration and hence, the BC-Au-DAPT nanocomposite system is an encouraging platform for the treatment of superbug-infected wounds.

Majeed et al. [30] biochemically employed Penicillium decumbent (MTCC-2494) for the extracellular biological production of silver nanoparticles. The formation of a dark brown color in the conical flask indicated AgNPs production. The AgNPs produced were characterized by UV-Spectrophotometric analysis, which revealed optimum absorption value at 430 nm which confirmed the presence of nanoparticles, while FTIR analysis revealed amines and amides as the possible proteins involved in the stabilization of the nanoparticles as a capping agent. They also reported that AFM and FESEM confirmed that the particles were spherical in shape and roughly surfaced nanoparticles with sizes of between 30 and 60 nm. They concluded that the biosynthesis procedure was discovered to be fast, eco-friendly and financially savvy and that AgNPs were discovered to have extensive antimicrobial activity and also it showed good enhancement of antimicrobial activity of *Carbenicillin, Piperacillin, Cefixime, Amoxicillin, Ofloxacin* and *Sparfloxacin* in a synergistic mode and that the AgNPs displayed suitable anticancer activity at 80 $\mu g\ mL^{-1}$ after 24 h of incubation and that the poisonousness increases after 48 h of incubation against A-549 human lung cancer cell line and the synergistic preparation of the antibiotic with the nanoparticles synthesized was discovered to be increasingly compelling against the pathogenic bacteria investigated.

7 Green Polymer Nanocomposites for Sensors, Catalytic and Energy Applications

No doubt, cellulose is the utmost available natural polymer and it gives a viable green asset, which is: sustainable, degradable, biocompatible and financially savvy. Of late, nanocellulose-based mesoporous structures, adaptable thin films, fibers and networks are progressively being manufactured and utilized in photovoltaic gadgets, energy storage systems, mechanical energy harvesters and catalyst components, henceforth exhibiting the huge materials science esteem and application potential in numerous energy-related fields. There are progressions in the utilization of biopolymers, especially, cellulose, in the areas of a photovoltaic (PV) module and mechanical energy harvesting is reviewed. Particularly, for PV module, promising uses of cellulose-based nanostructures for PV encapsulates and photo-electrochemical electrodes advancement are on the increase. For mechanical energy collection, the latest innovation advancement in cellulose-based triboelectric nanogenerators is likewise conceivable. Therefore, the upcoming prospective research and prospects of cellulose nanomaterials as a novel energy material can only be expanded. The benefits of cheap and comparatively great safety of sodium-ion batteries (NIBs) have made them attractive, hence promising candidates for large-scale energy storage systems. The drawback being their inherent low energy density to lithium-ion batteries needs to be investigated and optimized. There is the need to work on the grid-level energy storage applications, designing and finding suitable anode materials for NIBs, which are of great concern. Despite the good attempts on the advancements and novelties realized, numerous contests, such as stumpy energy/power densities, modest cycle performance and the poor initial Coulombic efficiency, still limit the current requirements of the large-scale application. It is envisaged that sophisticated nanostructured approaches for anode materials can drastically improve ion or electron transport kinetic behavior, therefore enhancing the electrochemical characteristics of battery systems.

Gold nanoparticles (AuNPs) using *guar gum* (GG) as a reducing agent were also synthesized by Pandey et al. [32] via affordable biodegradable method. They characterized the particles obtained by UV–vis spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). Their observations showed a possible mechanism for this method of AuNPs synthesis. They therefore exploited the GG/AuNPs nanocomposites (GG/AuNPs NC) for optical sensor for detection of aqueous ammonia based on surface plasmon resonance (SPR). They concluded that the (GG/AuNPs NC had good reproducibility, response times of ~10 s and outstanding sensitivity with a detection limit of 1 ppb (parts-per-billion) and that the system allowed the fast fabrication of an ultra-low-cost GG/AuNPs NC-based aqueous ammonia sensor. El-Sherbiny et al. [10] described the production of new core-shell amino-terminated hyperbranched chitosan nanoparticles (HBCs-NH_2) NPs for optical sensor application. They characterized the nanoparticles by means of ninhydrin assay, FTIR, TGA and FESEM and then used the nanoparticles as platform for facile and controlled synthesis of silver nanoparticles (AgNPs),

which was established by using FTIR, UV-vis spectrometry, X-ray diffraction, SEM and HRTEM. They then used the newly (HBCs-NH_2) synthesized NPs as a platform for facile and controlled synthesis of silver nanoparticles (AgNPs) which were confirmed using FTIR, UV-vis spectrometry, X-ray diffraction, SEM and HRTEM.

An easy green synthesis of stable silver nanoparticles in flower concentrate of *Acmella oleracea* and its dopamine detecting properties were described by Raj et al. [36]. UV-visible spectroscopy, Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM) and particle size analysis were carried out to establish the formation of silver nanoparticles. They concluded that the response time of the sensor is 6 min and the detection limit is 2×10^{-7} M.

8 Future Prospects/Trends

Without a doubt, in the last two decades, there have been exciting and phenomenon advances in the study of microorganism-manufactured nanoparticles field and its usages. Despite these advancements, there is still enormous work required to enhance on the synthesis efficacy and the particle size control and morphology. Synthesis period reduction will significantly make the biosynthetic pathway considerably, more attractive. In the evolution of nanoparticle synthesis, particle size, size distribution and monodispersity are important concerns that need good attention. Since nanoparticles produced by microorganisms are subject to decomposition after a certain period, therefore, it is pertinent that the stability of nanoparticles developed by biological approaches should, as a matter of importance, elicit further study and this investigation should be a subject of high priority. Biological processes with the potential to meticulously control particles synthesized via chemical and physical methods require good control of particle size and shape/morphology. In order to acquire good control of nanoparticles obtained via plants (biosynthesis), parameters, such as: synthesis conditions, microorganism, type microorganisms, growth stage of microbial cells, reaction time, substrate concentrations, growth medium, pH, source compound of target nanoparticle, temperature and addition of non-target ions may require being varied and further studied.

Since nanoparticles might be coated (when required) with a lipid layer that gives physiological solvency and strength, which is basic for biomedical applications and is the bottleneck of other manufactured strategies, biosynthetic techniques are, hence, beneficial. It is foreseen that little response time and higher union viability can be accomplished when there is a superior comprehension of the blend component on atomic and cell levels, which should include the identification and isolation of the compounds that are the main reason for the decrease of nanoparticles.

9 Conclusion

Even though not every particles utilized for therapeutic purposes fully conform with most recent recommended and the commonly recognized description of nano size, this does not essentially have an adverse effect on their usefulness for restorative purposes. The explanation behind this is on the grounds that these nanoparticles (NPs) are appealing for the motivations behind medical applications dependent on their unique and important features, like surface-to-mass proportion that is significantly higher than that of different particles, quantum properties and the capacity to adsorb and carry other compounds. Most nanoparticles, generally, have moderately enormous and useful surfaces that are capable of adsorbing, binding and carrying other compounds, like: proteins, drugs and probes, even though many challenges still need to be survived, if the use of nanotechnology is to bring more sophisticated diagnostic opportunities, understand the expected enhanced comprehension of the pathological and physiological bases of ailment and yield enhanced treatment.

The most sought-out nanomaterials for several applications, such as: various biomedical applications, antimicrobial and antibacterial, electronic and catalytic applications, are gold nanoparticles. The comprehension of the extraction of gold nanoparticles utilizing plant extracts is of great importance. The production of gold nanoparticles from plant extract is beneficial, because of its decreased natural worries as well as on the grounds that it very well may be utilized to create significantly extensive amounts of nanoparticles and plant extracts effective as reducing agents and at the same time, stabilizing agents in the synthesis of nanoparticles, in general and gold nanoparticles in particular. Since it is highly biodegradable and very easy to use, with varied applications with the preferred particle size and shape, the synthesis of gold nanoparticles by using plant extracts has an advantage over the other physical methods, while plants have enormous potential for the manufacture of gold nanoparticles. Several biological substances, such as: gelatine, albumin and phospholipids for liposomes and several materials with chemical nature, such as: polymers and solid metal substrates, encompassing nanoparticles, are also presently being studied for the preparation of nanoparticles for drug delivery. The interaction of nanoparticles with tissues and cells and of course the possible injuriousness depends largely on the real composition of the nanoparticle and formulation; therefore, careful safety assessment of the nanoparticle formulations for drug delivery is of paramount importance. The pharmaceutical use and the recent requirements may be sufficient for the detection of most of the unfavorable effects of the formulations of nanoparticle; however, it cannot be envisaged that most features of nanoparticle toxicology can easily be identified.

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Chapter 14
Biopolymer Composites and Bionanocomposites for Energy Applications

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1 Introduction

The need for material improvement, new materials and environmentally friendly materials has necessitated the use of biomaterials, especially for the plastic-based materials. These environmentally friendly materials can be sourced from biomaterials (e.g., biopolymer, natural fibers, bio-nanoparticles, etc.). Talking about biopolymers, it is an alternative to the petroleum-based polymer and polymers from natural sources. The various natural sources will be explained in detail in the subsequent sessions of the chapter. On the other hand, as shown in the latter part of this chapter title, application of these materials in the energy sector has dominated the global community. The increasing energy demand, fossil fuels scarcity, alternative and renewable energy, climate change and population growth have contributed to the global energy

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research. The type and weight of material have a way of the contributions to the energy efficiency (energy generated and/or energy consumed) of the system. The properties such as thermal stability, impact strength, tensile strength, permeability, moisture resistance and flame retardance of biopolymers are inadequate for certain applications either in the automobile, packaging, construction, electrical and electronics industries. These setbacks can be overcome by reinforcing it with fibers, nanoparticle, hybridization, polymer blending just to mention a few.

Polymers are sometimes described based on the function, these descriptions include (i) conducting polymer composites or nanocomposites (significant for fabricating transient and flexible devices and materials used in electronics, robotics, intelligent, biomedical and military applications and (ii) smart polymer composites (better if they are biodegradable, biostable and biocompatible) [75]. The shift to "green energy" is of great importance to the global community, which resulted in different researches involving biodegradable polymer composites and nanocomposites. Materials like plastics, rubbers and adhesives are made from different arrays of synthetic polymers. The growing reliance on synthetic-based polymers has led to a number of human and environmental health concerns; because the production of some of these polymeric materials involves using toxic compounds or the creation of by-products that are toxic in nature. The detrimental health and environmental impacts caused by synthetic and petroleum-based polymers are gradually advancing, generating worldwide concern. The hazardous impact of these materials is due to the non-biodegradable nature and the way they were obtained, which is from non-renewable resources. Furthermore, the increasing use of synthetic polymers has contributed to deteriorating the environment. Hence, leading to the movement by activist, laws and policies by government and consumers interest in an environmentally friendly product that possesses similar qualities to those products made from synthetic polymers [4]. The possible depletion of fossil fuel (coal, oil and natural gas), technological advancement, create innovative ideas and discovery of materials has accelerated the progression into biobased polymers and products.

Biobased refers to polymers produced from raw materials that are renewable. The polymers from such renewable sources are termed to be biodegradable polymers (sometimes called biobased polymers). Biodegradable polymers are materials which when acted upon by bacteria and microorganisms, it deteriorates and degrades completely back to the environment without any harmful effect. There has been a tremendous growth in recent years for biobased polymers due to technological advancement and various commercial applications of biopolymers. There exist three major ways of producing biobased polymers from renewable resources [4]:

i. Then use of natural biobased polymers with partial modification to meet the requirements.
ii. Synthesizing biobased polymers directly by bacteria, an example is polyhydroxyalkanoates (PHA).
iii. Making biobased monomers by fermentation or traditional chemistry followed by polymerization, an example is a polylactic acid (PLA).

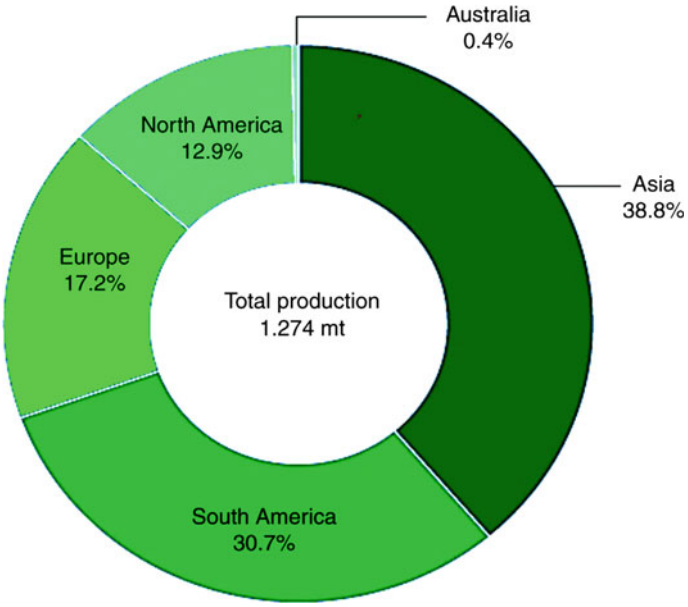

Fig. 1 The production capacity of biopolymer per geographical regions dated 2012. *Source* [91]

Many of these biopolymers are currently being used in areas like packaging, electronics, biomedical just to mention a few. The inherent physical and chemical properties coupled with the little or neutral negative environmental impact of these materials have contributed to the current interest. This trend is envisaging to continue. Many research works have been reported based on the topic of discussion, the review article highlight and summarized the use and importance of biopolymer composites and nanocomposites in different fields which include the energy sector. The chapter will discuss various applications, selection, desired properties and the future trends of biopolymers in the current age and time. Production rate region is shown in Fig. 1.

2 Types of Biopolymers

Biopolymers are products or natural renewable resources from the living organism; this can be from starch, cellulose, lignin, hemicellulose, soy protein, chitosan and collagen or synthetic biopolymers [76]. Biopolymers being from living organisms can be referred to as polymeric biomolecules. The fact that it is a type of polymer; it contains covalently bonded monomeric units, forming larger structures. There exist three major classes of biopolymers, which are classified based on the monomeric units used and the structure of the formed biopolymer. The structural biopolymers

Table 1 Classification of biopolymers based on the source of origin

Microorganisms	Bioresources	Chemical synthesis
Polyester (PHB, PHBV)	Lipid (wax, fatty acids)	Biomass (PLA)
Carbohydrate (pullulan, curdlan)	Protein (gelatin, corn zein, wheat gluten)	Petrochemicals (PGA, PVA, PCL)
	Carbohydrates (starch, chitosan, agar)	

Source [56, 60]
PHB Polyhydroxybutyrate, *PHBV* Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), *PLA* Poly(lactic acid), *PGA* 2-Phosphoglycolic acid, *PVA* Poly(vinyl acetate), *PCL* Poly(ε-caprolactone)

include the following and are shown in Fig. 2. Another alternative way of classifying biopolymers is presented in Table 1.

i. Polypeptides: They are short polymers of amino acids.
ii. Polysaccharides: They are mostly linear bonded polymeric carbohydrate structures, having long chains of monosaccharide units firmly joined together by a glycosidic bond.

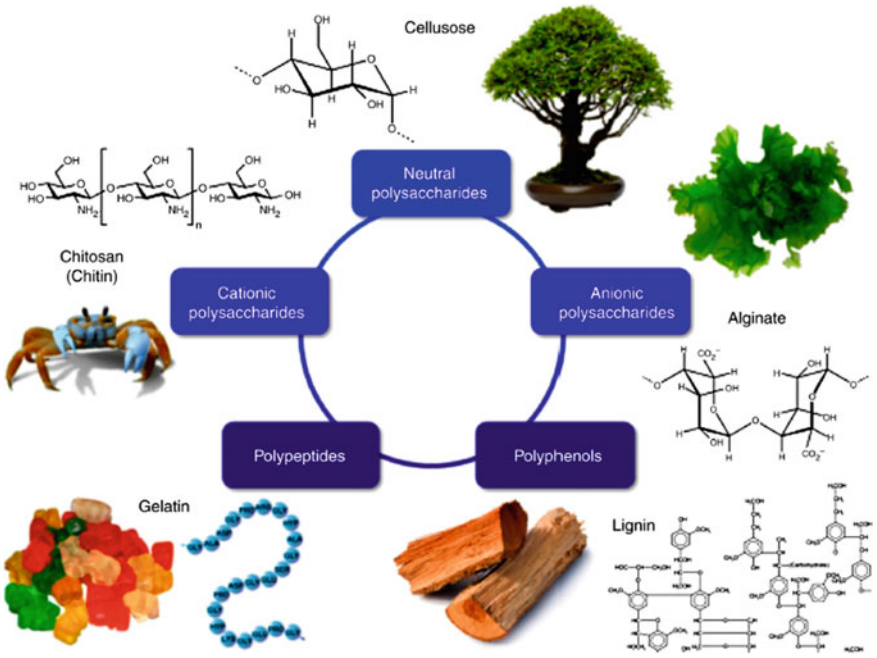

Fig. 2 Structural biopolymers. *Source* [76]

iii. Polyphenols: They are a structural group of mostly natural, synthetic or semisynthetic and organic chemicals which are characterized by the existence of large multiples of phenol structural, it is also known as polyhydroxyphenols.

According to Kim [48], one of the most abundant biopolymers in nature is cellulose, which happens to be the main chemical constituent in plant fibers [56]. Cellulose is known to possess fascinating properties and structure [62]. Some of the properties include renewability, biodegradability, inexpensiveness and biocompatibility [69]. The derivatives are useful in many applications not limited to coatings, immobilization of proteins and antibodies, laminates, pharmaceuticals, optical films, foodstuffs, textiles, the formation of cellulose composites (with synthetic polymers and biopolymers) and so on. The two morphologies of naturally occurring cellulose are in the amorphous and nanocrystal domains [48]. The structural hierarchy of cellulose extracted from plants (wood) is shown in Fig. 3. Detailed explanation about the components of wood can be found in a research work by Kim [48]. Cellulose particle types are in four main categories which are differentiated by the aspect ratio, characteristic dimension, morphology and crystal structure. These categories are (i) microcrystalline cellulose (MCC), having high crystallinity [38], (ii) microfibrillated cellulose (MFC), with an aspect ratio of 10–100 nm wide and 0.5–10 μm in length [87], (iii) nanofibrillated cellulose (NFC), with an aspect ratio of 4–20 nm wide and 500–2000 nm wide [1], and (iv) cellulose nanocrystals (CNC), with an aspect ratio of 3–5 nm wide and 50–500 nm long and highly crystalline (54–88%) [28]. Biopolymer global production capacity as at 2009 and 2011 was 766,000 and 1.5 million metric tons, respectively. Figure 4 shows the bioplastic annual production within a period of 2007–2011.

3 Nanobiocomposites

Nanotechnology is an alternative method for enhancing the physical and chemical properties of polymeric materials. The introduction of a component in nano-size (i.e., at least one of the dimension is <100 nm) into a matrix (metal, ceramics or polymer) makes the overall new material to assume the name nanocomposites. The use of nanoparticles as reinforcement in polymeric materials has shown great improvement in physical, thermal and mechanical properties. Nanoparticles are classified based on their chemical nature, physical structure, size and shape, but the main classification is based on the particle shape. The incorporation of nanoparticles into biopolymers led to the development of bionanocomposites. According to Fischer [31], biopolymer-based nanocomposites have shown improvement in thermal stability, barrier properties and tensile strength. These properties are the most desired in any composites or nanocomposites. The methods of preparation of nanocomposites include in situ polymerization, solution and melt dispersion, solgel synthesis and self-assembly [25].

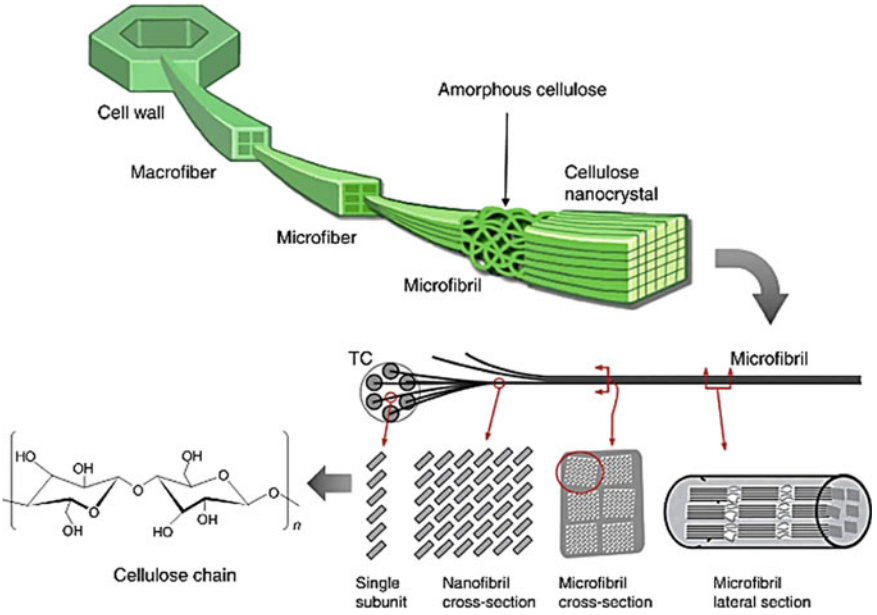

Fig. 3 Structural hierarchy of cellulose. *Source* [48]

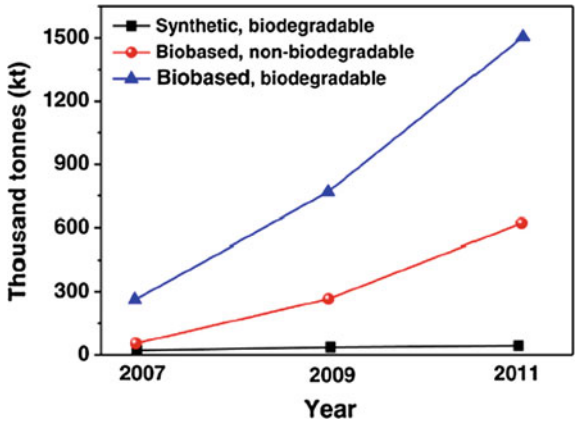

Fig. 4 Bioplastic annual production between 2007 and 2011. *Source* [76]

4 Applications of Biopolymer

The properties of composite materials have made them have various useful applications. Several kinds of literature have pointed the importance of polymeric composites and nanocomposites (in this case, biopolymers) for the sporting and gaming industries, medical sector, packaging industries and in the field of electronics [60, 84]. Sporting equipment made from composite materials, generally makes the usage

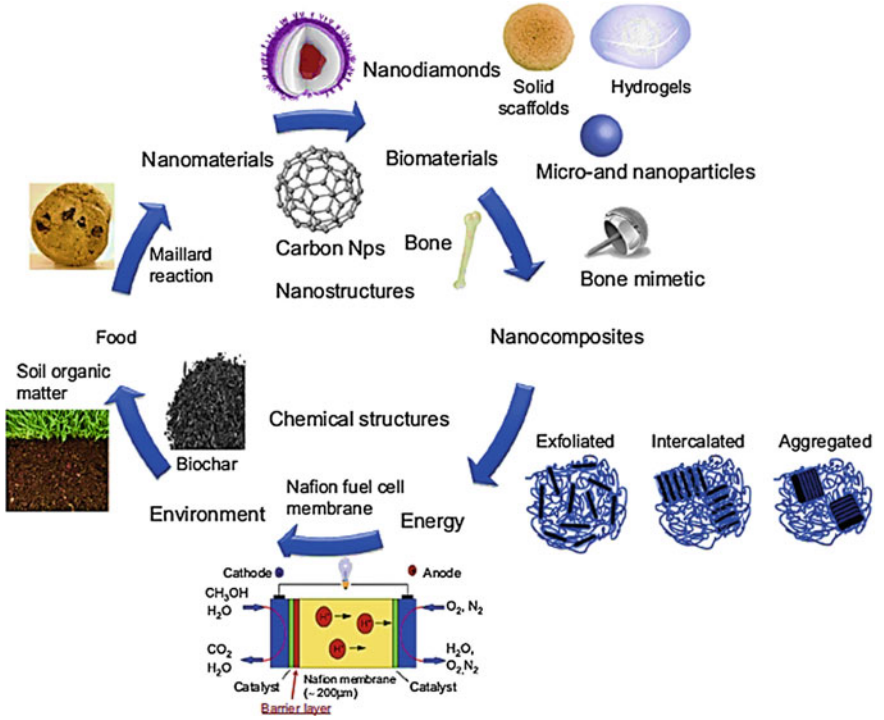

Fig. 5 Areas of applications of nanocomposites. *Source* [84]

enjoyable and convenient without much stress due to the strength and lightweight. Materials like tennis kayaks, rackets, boats and several other sports equipment are made from polymeric, fiber, nanoparticles and so on. The polymeric materials used can be a biopolymer in the case of the medical implant where the material should be non-corrosive, non-toxic, biodegradable and biostable. For the past five decades, research focus has been on synthesizing biomaterials for medical dental implants for the treatment of millions of patients annually [84]. The material can be in a form of the composite which can further be improved upon by reinforcing with a nanoparticle leading to a different kind of materials called bionanocomposites. Similar materials have been utilized in the food packaging and electronic industries [60, 66]. Figure 5 shows the application of nanocomposites in various spheres of life.

4.1 Electronics

There has been a great improvement and new materials used for the fabrication of electronic devices. A large amount of these materials has been from polymer

composites and nanocomposites. The level of research has greatly increased the use of biopolymers for electronic composites materials and devices. A large number of research works has been published on the various applications of biopolymer-based composites for the fabrication of actuators, sensors, electromagnetic shielding materials, supercapacitors, microwave absorbers, just to mention a few [46, 48, 53, 65, 85]. Conjugated polymeric materials with different inclusions of nanoscale filler have been reported for sensor applications, which include biosensors, gas sensors and chemical sensors. The nanoparticles employed include carbon nanotubes (CNTs), metal oxide nanowires, nanoscale gold, silver, copper, nickel, palladium particles and platinum [37].

Polymers, composites and nanocomposites are largely consumed in the field of electrical/electronic this day [77]. Biopolymers have gradually found their way into this space due to the environmental threats posed by non-biodegradable, non-renewable and non-environmentally friendly synthetic polymers. This unique material has been widely used for different electrical components and devices [3, 14]. Muthumeenal et al. [63] explain the use of biopolymer for the development of fuel cells. In their report, polymer electrolyte membranes (PEMs) were developed. PEM is known to offers high energy density and high efficiency. Fuel cells are distinguished from each other by the electrolyte material. A schematic diagram of a PEM fuel cell is shown in Fig. 6. Utilization of biopolymers for polymer electrolyte membrane fuel cells (PEMFCs) contributes to greening the environment as less CO_2 is released into the atmosphere.

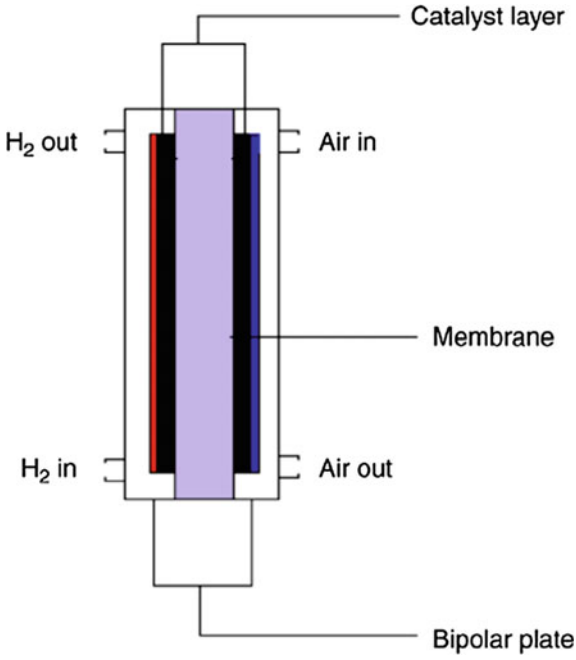

Fig. 6 Schematic diagram of polymer electrolyte membrane fuel cell. *Source* [63]

PEM fuel cells are not the only fuel cell products developed from biopolymer, others include hydrogen-polymer electrolyte fuel cells (PEFCs), alkaline fuel cells (AFCs), microbial fuel cells (MFCs) and direct methanol fuel cells (DMFCs) [96]. The durability and efficiency of AFCs can be largely enhanced by using an anion exchange membrane. Different degrees of deacetylation and various molecular weights of chitosan membranes were developed and recommended as a suitable candidate for AFC applications [98].

Biopolymer matrix has been reinforced with different conductive micro- and nanoparticles metals to produce composite and nanocomposite materials for various scientific applications [16, 71, 74]. Such polymer combines both the properties of the metals and the polymers to form a conductive polymer. The electrical conductivity and other properties of the developed materials are greatly influenced by the particle shape, size and quantity that are incorporated [72, 103]. Among all the metal nanoparticles, silver has the most electrical conductivity and thermal properties, which is the reason it has found useful applications in electronics [47] and antimicrobials [89]. Table 2 shows various conductive polymers and their respective thermal conductivity.

Abdo et al. [3] presented the behavior of electrical conductivity of biopolymer-based nanoparticle. From their report, it was concluded that biopolymers on its own natural properties are not conductive but acquire conductive properties through the influence of the added conductive metal. Combine properties of bionanocomposites being renewability, biodegradability, biocompatibility, biostable, carbon neutral and electrical conductivity have made biopolymer-based composites and nanocomposites an environmentally friendly material.

A similar observation was reported by Bhakat et al. [14], where they prepared biopolymer nanocomposites, having Gum Arabic as the host and Fe_3O_4 as the guest. Non-extrinsic type of semiconductor nanocomposites was formed. The electrical conductivity of the materials developed increased with increasing nanoparticle content, while the activation energy decreased simultaneously. The conduction mechanism of the bionanocomposites is dependent on the charge carrier transferred by the nanoparticle molecule collections, distributed in the biopolymer matrix.

Thermoelectric effect is a process of transforming heat energy into electrical energy. The thermoelectric materials efficiency is based on its ability to conduct electrical energy and not heat (thermal energy). Thermoelectric materials are specially designed to increase the electrical conductivity without any visible change in the thermal conductivity. The thermoelectric material's performance can be determined by the parameter known as thermoelectric figure-of-merit (ZT) as shown in Eq. (1).

$$\mathrm{ZT} = \left(S^2\sigma\right)T/k \tag{1}$$

where

ZT is the thermoelectric figure-of-merit (dimensionless);
T is the absolute temperature;

Table 2 Conductive polymers

Polymer	Abbreviation	Thermal conductivity (S cm^{-1})
Polypyrrole	PPy	10^2–7.5×10^3
Polyaniline	PANI	30–200
Poly(3,4-ethylenedioxythiophene)	PEDT, PEDOT	–
Polythiophene	PTh	10–10^3
Polythiophene-vinylene	PTh-V	–
Poly(2,5-thienylenevinylene)	PTV	–
Poly(3-alkylthiophene)	PAT	–
Poly(p-phenylene)	PPP	10^2–10^3
Poly(p-phenylene-sulfide)	PPS	–
Poly(p-phenylenevinylene)	PPV	$3–5 \times 10^3$
Poly(p-phenylene-terephthalamide)	PPTA	–
Polyacetylene	PAc	10^3–1.7×10^5
Poly(isothianaphthene)	PITN	–
Poly(α-naphthylamine)	PNA	–
Polyazulene	PAZ	–
Polyfuran	PFu	–
Polyisoprene	PIP	–
Polybutadiene	PBD	–
Poly(3-octylthiophnene-3-methylthiophene)	POTMT	–
Poly(p-phenylene-terephthalamide)	PPTA	–

Source [11, 21]

S is the Seebeck coefficient;
σ is the electrical conductivity;
k is the thermal conductivity.

When materials have similar thermal conductivities, the performance of thermoelectric can be determined by the power factor (PF) shown in Eq. (2).

$$\mathrm{PF} = \left(S^2\alpha\right) \tag{2}$$

Arrhenius equation explains the temperature dependence of conductivity for conducting substances, and accordingly, the value of activation energy is low for the highest conductivity; see Eq. (3).

$$\sigma = \sigma_o \exp(-E_a/kT) \tag{3}$$

where

σ is the electrical conductivity;
σ_o is the preexponential factor;
E_a is the activation energy;
k is the Boltzmann constant.

Thermoelectric properties (electrical conductivity, thermal conductivity and thermopower) of biopolymer composites measured at room temperature, is a function of the different modification that is performed, such as polymer blending, nanoparticle inclusion, plasticizer or dopant. The use of biopolymers for a thermoelectric generation will help resolve the energy crisis and create sustainable energy from bio-renewable resources. Mohiuddin et al. [61] also showed that photovoltaic and photodetector materials can be produced with biopolymer-based composites and nanocomposites. Light-emitting diodes and microwave absorbers have equally been developed from biopolymer composites, respectively [36, 80].

Abdo et al. [3] reiterated the growing interest of biopolymer for applications in food packaging, bioplastics, electronics, medicine and coating, due to basic characteristics and most importantly, biodegradability and electrically conductive. However, some limitations have been reported concerning conventional biopolymer regarding their electrical properties, because biopolymer alone is non-conductive. The inclusion of nanoparticles into a biopolymer matrix helps to enhance the electrical conductivity making it differ from the unreinforced biopolymer. Therefore, nanoparticle type and particle loading have a direct impact on the overall electrical conductivity properties of the nanocomposites and have been produced for this purpose. Kim [48] further investigated the impact of nanoparticle on creating multifunctional smart biopolymer composites for actuators. The functionality of the materials is improved by incorporating graphene, carbon nanotubes, tin oxide, metal nanoparticle and titanium dioxide into the biopolymers. Due to the inherent properties of biopolymers (biostable, biocompatible, biodegradable), it can be used for various actuators like biomimetic robots, reconfigurable lens systems, artificial muscles, just to mention a few.

Cyprych et al. [20] reported the possibility of applying starch as a dye-doped bio-polymeric matrix which is designed for a random lasing generation. The photostability of laser emission of starch biopolymer-based systems has experienced a significant increase when compared to other biopolymer-based composites without starch. This phenomenon has been explored for enhanced biomaterials. The authors further concluded that starch as a material can successfully be a medium for the random lasing experimental system. Similarly, the fully functional material used for photonics applications can be made from starch, making it possible to develop biological photonic devices [94].

Singh et al. [86] presented a paper titled "solid gellan gum polymer electrolyte for energy application." From their work, solid gel electrolyte synthesis was developed from carbohydrate polymer based (Phytagel/gellan gum). This material could be used in the dye-sensitized solar cell (DSSC). The authors further explain the influence of potassium iodide (KI) in Gelrite/Phytagel biopolymer to produce solid gel electrolyte. Figure 7 shows the ionic conductivity of the biopolymer-based electrolyte.

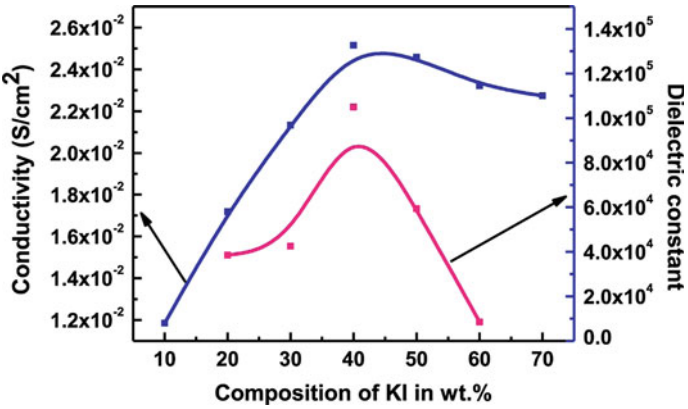

Fig. 7 Influence of KI composition on ionic conductivity of Phytagel doped with KI system. *Source* [86]

The inclusion of KI in the matrix (Phytagel) improved the ionic conductivity and the interaction between KI and the biopolymer matrix due to the mobile charge carrier increased. Reduction in ionic conductivity after the optimum value of approximately 2.45×10^{-2} S/cm^2 is as a result of multiple ion formations.

Biopolymers have been widely used in recent time in field-effect transistors (FET) in the areas of chemistry, physics, materials and microelectronics. The material application extends beyond the field of advanced biomedical devices to electrical/electronic materials, which makes the materials unique for electronic switches, storage devices, gates, biosensors and biologic transistors. A new class of biosensor technology has emerged, thanks to various opportunities created by FET-based biosensors. Hence, the FET-based biosensor can be used for clinical diagnosis, biomedicine and environmental monitoring. There are other useful applications of biodegradable polymers such as organic semiconductors (OSCs) and organic thin film transistors (OTFTs) [13, 22].

Technological advancement has led to the development of devices like supercapacitors (SC), which are used for applications where longer lifetime or a high number of charge/discharge cycle of the appliance is required. Other applications of SC are voltage-leveling functions (lead–acid batteries), consumer electronics, energy storage, grid power buffer and so on. Advantages of SC include the provision of back-up or emergency shutdown power, powering actuator indoor and evacuation slides in airplanes, energy storage for street lights, power split in the automotive industry. According to Okonkwo et al. [65], biopolymers are gradually being used to develop SC due to the large surface area, relatively good electrical conductivity and porous nanostructures (more ion adsorption and active sites for the charge transfer reactions). Biopolymer composite-based dielectric materials are designed to improve the efficiency of supercapacitors. In a similar report by Deshmukh et al. [26], various ways of improving the dielectric properties of biopolymer-based composites and

nanocomposites were discussed. Some of the approaches include a dispersion of nanoparticles into the biopolymers.

Haque et al. [36] discussed the use of biopolymer in electroluminescent devices, like light-emitting diodes (LEDs), display applications and optically pumped laser. With the advancement in this field, low-cost and environmentally friendly materials can be developed. The ease in processing method also contributed to the global attraction of biopolymers in electrical/electronic applications. This development has equally shifted to the fabrication of photovoltaic (PV) and photodetector devices made with biopolymer composites and nanocomposites [61]. PV converts light energy (ray) to electrical energy. Most PV is made from inorganic silicon wafers which are not environmentally friendly, hence, the reason for increasing research for biomaterial-based PV.

4.2 Packaging

Food packaging has attracted so much attention based on the standard that is required for materials used. The materials must be efficient enough to maintain the food quality and also the food safety. Furthermore, it should prevent unfavorable factors such as spoilage microorganisms, chemical contaminants, oxygen, moisture, light, just to mention a few [56, 93]. Food packaging materials should have good thermal, mechanical and optical properties because they act as a barrier against permeation of oxygen, water vapor, carbon dioxide and other volatile compounds. The quality of the packaging material has a direct influence on the quality of the packaged food. The packaging should maintain the quality of the food right from when it was packaged until the period of consumption by the final consumer. Figure 8 shows the life cycle of food packaging materials.

Biobased materials are currently being used for packaging due to the fact that they are eco-friendly, which serves as an alternative to the non-renewable petroleum-based

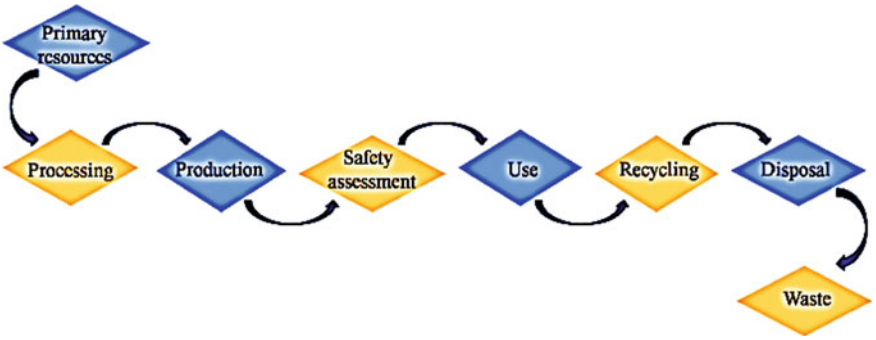

Fig. 8 Food packaging materials complete life cycle. *Source* [60]

packaging materials. Other advantages of using biopolymer materials for packaging over the petroleum-based materials include biodegradability, readily available and low cost. The drawback associated with biopolymer materials for packaging applications is poor mechanical and water vapor permeable properties. Incorporation of nanoparticle will help resolve the drawback of biopolymers. Polymer-based bionanocomposites offers superiority over ordinary or unreinforced biopolymer composites. The improvement includes high mechanical, thermal, antimicrobial, gas and vapors barrier properties. The most suitable polymer bionanocomposites for food packaging are those made up of starch, polycaprolactam, chitosan, polylactic acid, polyhydroxy butyrate, poly(butylene succinate), etc. while the appropriate nanoparticles for these matrices are montmorillonite and kaolinite. In addition, certain smart materials can be incorporated to achieve antimicrobial, sensor, oxygen-scavenging properties [60].

In the recent time, biopolymers, being a biodegradable product, are considered for packaging materials due to the fact that they can easily degrade by the environment and on burning does not produce gases that are harmful to human, plants and animals. On record, approximately 40% of food packaging materials (films, bags, cups, plates, bottles, sheets, tubs, trays and so on) are made from plastics. These plastic materials, if not biodegradable, possess a serious threat to the environment. The harmful nature of non-biodegradable packaging materials is a global concern in recent time. Therefore, researchers are making considerable efforts to resolving the crisis posed by such materials. To achieve these objectives, the intended material must meet the minimum requirements shown in Fig. 9 and other regulations that come with the use of such materials. Another interesting thing about biopolymers is that additives like antimicrobial agents, antifungal agents, antioxidants, colors and other nutrients can be added easily [35, 43]. Biopolymers are considered good materials for packaging, but it has its own limitations when they are used without any filler/reinforcement. Biopolymer-based materials are known to be highly hydrophilic in nature, with low mechanical strength. There have been many types of research on how to improve on these limitations [7, 70, 78, 81]. The quest for improvement brought about materials known as bionanocomposites because the source is a biodegradable-based polymer and nanoparticle inclusion. Bionanocomposites have improved mechanical, barrier, thermal, rheological and antimicrobial properties [10, 49].

Packaging materials exist in four different types and it includes (i) conventionally used one—it has no barrier layer, (ii) passive barrier multi-packaging materials which is reinforced with nanoparticle to form nanocomposite film with high barrier property at the middle, (iii) active barrier multi-layered packaging materials having gas scavenging molecules' layer at the middle just like the passive type and (iv) passive-active barrier multi-layered food packaging materials having a layer of nanocomposite materials at the middle with improved barrier property sandwiched with a gas scavenging material layer. An illustration of the schematic diagram is contained in a report titled "*Bionanocomposites for food packaging application*" by Rhim et al. [82].

The essence of using bionanocomposites and not just biopolymer or composites alone is due to the inability of the passive barrier packaging materials to prevent the

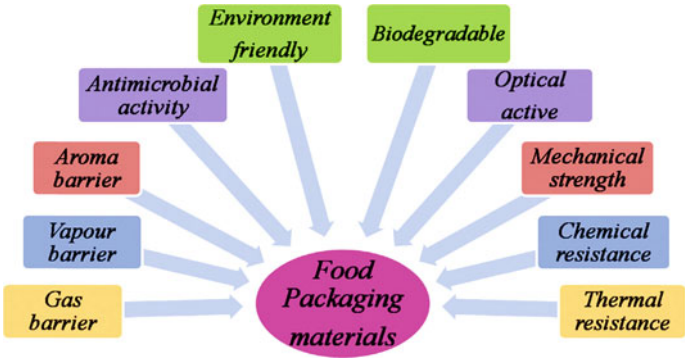

Fig. 9 Basic requirements for food packaging materials. *Source* [60]

passage of oxygen or remove residual oxygen in the wall of the material package. Hence, causes various deterioration reactions like nutrient losses, microbial growth, color and flavor change, change in respiration rate and production of ethylene in vegetables and fruits. The active barrier packaging materials can prevent the above-mentioned drawbacks associated with passive packaging materials. The problem of possible growth of anaerobic bacteria can still occur at a later stage. Hence, the need to introduce antimicrobial material into the bionanocomposites to control the growth of microbial during the post-processing period [9, 73, 93]. All of these processes will lead to a prolonged shelf life of the food packaging materials with an end result of material safety and food quality maintenance.

Another interesting aspect of food packaging is the use of smart packaging materials. The approach can assist in predicting the packed food quality and the surrounding environment [104]. The creation of the smart packaging materials is achieved by manipulating and controlling the particle (nanoclay) size and functionalizing with various organic functional components. This gives useful information about leak indicator for the packed foods, enable tracing the origin of food packaging material (radio frequency identification) and product time-temperature history (time-temperature indicators) [33, 82].

4.3 Biomedical

Advancement in the medical field has led to the use of foreign materials in the human body. This technological improvement and innovative ideas have shown that defected human body part can be replaced with biodegradable, biostable, non-toxic and non-corrosive materials. This replacement is done in the form of implants which is carefully done in order to avoid any negative effect it may have on the human health. Areas in the medical field where this has been done include dental applications, drug delivery, tissue engineering, orthopedic applications, wound-dressing and biosensor

applications [84]. The human teeth are known to be the hardest component in the human body, internally or externally, next to it is the human bone. This is due to the chemical and structural makeup, consisting of hydroxyapatite [$Ca_5(PO_4)_3(OH)$]. In a report by Saini et al. [84], it was stated that over 100 million people are missing their teeth, making the need for a dental implant to be very high. The report was an extract from the report published by the National Institutes of Health (NIH), a US Department of Health and Human Services (DHHS) agency.

The vacuum created calls for researching various materials that can meet the laid down standards by the National Bureau of Standard of the US government. Among the materials that met this standard is polymer-based composites and nanocomposites, due to the various properties, easy processing conditions, compatibility with the human body and availability. Consideration of biopolymer-based composites for restorative materials, denture bases and teeth, dental cement and implants must take into account elevated temperature, atmospheric oxygen and electromagnetic radiation to which it may be exposed to.

Bone is composed of an organic-inorganic complex of 60, 30 and 10%, mineral (nanohydroxyapatite), matrix (collagen, a major structural protein of connective tissue) and water by weight, respectively, and it is a natural extracellular matrix (ECM). Bones form a shield for the internal organs and marrow, good structural framework, mechanical strength, regulation of blood pH, maintenance of the phosphate and calcium level for the metabolic processes and store ions required for the body to function normally, and it is a major part of endoskeleton of all vertebrates. Hence, properties such as high strength and elasticity are required [18, 32, 90, 97]. Injuries related to bone fracture and grafting are a global occurrence, cutting across all ages from childhood to adulthood. Addressing this occurrence requires materials that can either repair or replace the affected bone. According to Ibrahim et al. [41, 42], the material should be biodegradable, non-toxic, biocompatible, biostable and meet the minimum specification for which it is intended because of the direct contact it has with the human body. Studies have been around the use of hydroxyapatite [$Ca_5(PO_4)_3(OH)$] for bone repair and implantation. Hard tissue and undesirable mechanical properties are exhibited by hydroxyapatite, therefore, biopolymer-based matrix reinforced composites are required for effective performance of the bone repair or implant. Polysaccharides, polypeptides, collagen, chitosan (natural polymer) or biodegradable synthetic polymers are mostly used as a matrix for such applications.

4.4 Drug Delivery

Technology into drug delivery is one of the wider areas of science, which consist of a multidisciplinary scientific approach and contribute significantly to the improvement of health care. Adequate drug delivery approach to patient has helped to tackled chronic illnesses or acute diseases for several years. The conventional approach and routes of drug administration influence the rate of drug uptake which is controlled by the properties (solubility, molecular size, charge, etc.) of the drug. Advancement in

technology has greatly influenced the use of polymeric composites in biomedical or biotechnology. This has been researched further, involving the use biopolymers and nanoparticles, which is advantageous for drug delivery due to the formation of the effective barrier and sustained delivery having little or no burst release [19]. Biopolymer matrix nanocomposites have attracted much attention for drug delivery/release.

Nanoparticle inclusion creates a barrier for drug release giving rise to slower and controlled release and improves the mechanical reliability of the hydrogel-based bionanocomposites. Addition of nanoparticles like clay, silicate, graphene and carbon nanotube (CNT) has been reported in the literature [58, 59, 88]. Bionanocomposite for drug loading and release depend on the following conditions [6]:

(i) Chemistry of the nanoparticle (intercalation, hydrogen bonding or ionic interactions),
(ii) Content/amount of the nanoparticle in the composites,
(iii) Degree of dispersion and
(iv) Particle aspect ratio.

Biopolymer nanoclay composites offer various advantages like bioadhesion, film-forming ability and cell uptake. Loading of the drug onto clays can be improved and controlled by surface modification of the clays using various biopolymers. Kakran and Li [44] reported the utilization of CNTs over the existing drug delivery vectors, which is due to the ability to cross cell membranes easily, high aspect ratio and high surface area. Hence, provides multiple bonded sites for the drug targeting. Furthermore, CNT provides functionalization that can significantly lower the cytotoxic effects and increase the biocompatibility property. In addition, the functionalized CNTs have been proven to be safer than the pristine or purified CNTs. Thus, offering potential utilization of nanotubes for administering drug. Apart from having high-performance characteristics, the properties inherent to biopolymers such as biocompatibility and biodegradability open new prospects for bionanocomposite materials in medicine and environmentally friendly materials (green nanocomposites). Bionanocomposite materials are highly promising for regenerative medicine applications as drug-eluting materials, antibacterial coatings to protect surgical devices from biofilm formation, structural materials, coatings for vascular stents, wound-dressing materials with enhanced wound-healing potential and antibacterial coatings of public goods, among others.

Bionanocomposite-based polymeric materials with drug release properties hold immense potentials for wound-dressing applications, due to high water uptake, non-cytotoxicity, and high mucoadhesivity characteristics. Moreover, a wound-dressing material should be highly flexible, robust, elastic and tear resistance (self-healing) to bear the exerted forces by various body shapes and sizes. Many of these important requirements are fulfilled by different bionanocomposite as discussed previously, making them an ideal biomaterial for wound dressing [84].

Oliveira et al. [67] developed a hybrid system from the intercalation of 2-methyl-4-(4-methylpiperazin-1-yl)-5H-thieno{3,2-c}{1,5}benzodiazepine, also known as olanzapine (OLZ) in clay mineral. The low water solubility escalates the complexity

of dissolution and absorption of drug substances in the body, which affects the treatment of sicknesses and diseases [99] and has equally been proven to contribute to fatal intoxication in the body [64]. The presence of biopolymer-based bionanocomposites was shown to have controlled the drug release, improved bioavailability, and drug insolubility was reduced. Of all the material samples prepared, best performance was exhibited by the material comprising ratio 1:1 of ALG-XG (Alginate (ALG)—is a biodegradable and non-toxic polysaccharide extracted from brown algae while Xanthan gum (XG)—is a high molecular weight extracellular biopolymer produced by the fermentation of the gram-negative bacterium Xanthomonas campestris) [67].

In a review article by Park et al. [68], it was explained that the main reason while numerous biopolymer has been widely used for medical applications (novel biomaterials) is that of the easy processing, biodegradability and biocompatibility, which have equally been emphasized by various researchers. In their work, important information regarding different biopolymers and methods of preparing biopolymer-based composites and bionanocomposites including merit and demerit was extensively explained. Furthermore, various areas where functional biopolymers are currently in used were highlighted and they include bone, tissue engineering involving the skin, vascular graft, cartilage, implantable medical devices (barrier membrane and stent), drug delivery and so on. In a similar report by Davidenko et al. [23], the emphasis was made on two classes of biopolymers (polysaccharides and proteins) in respect to their biomedical applications for drug delivery system, wound management and tissue engineering scaffolds. The report also presented biomedical usage and properties of structural proteins with major emphasis on collagen. Collagen is largely used component for developing tissue engineered devices and various biomedical-based materials.

5 Environmental Impact of Biopolymer Composites and Nanocomposites

The annual production in the chemical industry worldwide is almost 300 million tons, of which the main outputs are plastics [57]. Plastics are essential in our day-to-day lives for a various component in the modern societies. Annually, there is a growing demand for polymer-based materials which has ripple effects on the environment, because most of this material ends up as environmental hazards either accumulating in the water body or landfill, contributing significantly to greenhouse gases emissions and many other undesired phenomenal. As much as polymer-based materials are important for many aspects of our lives, there are needs to consider the negative environmental impact as well. In order to overcome the negative impact of polymer waste, researchers are focusing on biodegradable polymers which could be from plant or animal as a replacement for non-biodegradable synthetic polymers.

The use of polymer-based materials in packaging has been questioned by consumer markets because of their negative environmental impact. Hence, the need to

develop alternatives, which are biobased. In a study conducted by de Léis et al. [24] in Brazil, Life Cycle Assessment was employed to analyze the energy and environmental performances of producing cassava starch-based film. The main observations of the research indicated that the impacts are majorly caused by the cassava crops, the fossil glycerine, manufacturing the film and ethanol additives used. Furthermore, energy and environmental impacts are interconnected with the cassava cultivation, consumption of electricity during manufacturing of film and the production of additives used in developing the film.

Biopolymers are produced from living organisms making it natural; therefore, it is termed eco-friendly. The nature of these eco-friendly materials has made them useful for wastewater clarification due to their flocculating and coagulating effects, hence, limiting the reliability on synthetic polyelectrolytes [45]. The removal of organic and inorganic wastewater pollutants has been made possible as a result of biopolymer hydrogels and nanocomposites films functioning as an effective biosorbents. Other important applications for biopolymer-based composites and nanocomposites are the following:

i. Removal of heavy metals and dye adsorption,
ii. Anti-desertification,
iii. Prevent leakages in concrete (natural biosealants),
iv. Conducting proton membranes for electrochemical systems and devices.

Environmental impact of biopolymers for various applications has been succinctly analysed, thus creating insight for the future prospect and applications for such materials. The environmental impact of biocomposites depends largely on the various components (polymer matrix, fiber, and nanoparticles) present in the composite and the nature (size, shape, dimension, etc.) of the various components. According to Korol et al. [52], eco-efficiency of the biocomposite and bionanocomposite materials are a function of the environmental effect of the material, which is determined by the Life Cycle Impact Assessment (LCIA). From their observation, there was a relationship between the eco-efficiency and the environmental impact categories that were considered.

Similarly, Guo et al. [34] studied the environmental burdens of a starch-polyvinyl alcohol biopolymer insulated cardboard cool-box under anaerobic digestion system. Several conditions were considered, but the combination of anaerobic digestion of the starch-polyvinyl alcohol biopolymer and recycling of the cardboard were observed to be superior environmentally. Furthermore, optimizing the energy utilization system can further bring about environmental benefits to the anaerobic digestion process.

6 Desirable Properties of Biopolymer Composites

The different properties of biopolymers include renewability, sustainability, nontoxicity and biodegradability. Several other properties make biopolymer of important

and useful materials for various applications. These properties range from mechanical, thermal, to biological properties. Improving any of these properties will further widening the area of applications by extending the durability, enhancing the environmental benefits and so on. Basically, the abovementioned properties can be improved by reinforcing with fiber [41, 42, 55], method of preparation [40, 92], polymer blending [5] and nanoparticle inclusion [39, 106]. A brief discussion about these properties is presented in the following subsections.

6.1 Mechanical Properties

Mechanical properties are among the most desired property for many composite materials. It defines the usage and area of applications. Several research papers have been published in this regard, and several more research is currently ongoing in enhancing the mechanical properties of biopolymer composites and nanocomposites. Bindhu et al. [15] prepared boron nitride (BN) reinforced PLA composites film for packaging. The BN content was varied; from their report, it was observed that 2 wt% BN (BN2) PLA composite showed optimum tensile strength. The improvement was as a result of proper dispersion of the particle in the matrix. A decrease in strength above BN2 reinforced PLA composites was due to agglomeration of the particle within the composites leading to the formation of cracks and further reducing the rate of stress transfer between the reinforcement and the matrix.

Yatigala et al. [105] studied the influence of reinforcing five different biopolymers with 30 wt% wood fiber. The biodegradable biopolymers are poly(lactic acid) (PLA), polyhydroxybutyrate (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), Bioflex (PLA blend) and Solanyl (starch-based). Maleic anhydride compatibilizer of 2–3 wt% was introduced to help enhance the interfacial interaction between the fiber and the polymer matrix. The compatibilizer was necessary due to weak fiber-matrix interaction, which usually leads to poor mechanical properties. There was improvement recorded for the mechanical and thermal properties of compatibilized wood fiber reinforced Bioflex, PLA, and PHBV. The improvements can be attributed to improved fiber-matrix interactions induced by the maleic anhydride. It was reported that compatibilizer showed no effect on Solanyl and PHB.

Rovera et al. [83] worked on thin film biopolymer loaded with cellulose nanocrystals (CNCs) and colloidal silica (CS) in the form of rodlike and spherical nanoparticles, respectively. The coated polymer was polyethylene terephthalate (PET). Larger particle size for CS improved the elastic modulus (8.19 ± 0.35 GPa), while the smaller particle size for the same nanoparticle showed better hardness (395.41 ± 25.22 MPa). In comparison, CS presented higher effect on the surface hardness of the coated PET than the CNCs; the recorded values were 353.50 ± 83.52 and 321.36 ± 43.26 MPa, respectively.

An and Ma [8] used the hot-pressing process to prepare green biodegradable composites comprising of wood fiber and poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P34HB) as the matrix. Maleic anhydride was incorporated as compatibilizer (coupling agent) to improve the interfacial adhesion between the fiber and the matrix. The mechanical properties were improved due to good interfacial interaction created by the coupling agent as a result of enhanced wettability of the fiber. Several other studies have been reported concerning mechanical properties of biodegradable composites and nanocomposites [12, 29, 30, 95].

6.2 Thermal Properties

Critical assessment of biodegradable composites/nanocomposites thermal properties would contribute further to understanding ways of improving the properties and, therefore, broadening the area of applications. Improved thermal properties enable the use of polymer-based materials for high-temperature applications like manifold, turbine blades, electronic components, just to mention a few. There are various ways of improving thermal properties of polymeric materials; they are a polymer blend, incorporation of fiber and coupling agent, nanoparticle inclusions, heat treatment, etc.

Abdelrazek et al. [2] prepared polycaprolactone (PCL) and polymethylmethacrylate (PMMA) biopolymer blend by casting technique. Thermal properties were studied by thermogravimetric analysis (TGA) as shown in Fig. 10. Pure PMMA was observed to possess lower thermal degradation properties, while PCL showed better result compared to PMMA. Blending PCL and PMMA together improved the equilibrium thermal stability of the overall composites. As the content of PMMA increased in the PCL matrix, the thermal stability was observed to decrease due to evaporation of moisture and stabilized at 120 °C. Major weight loss was observed within the range of 370–430 °C for all the prepared samples. Complete decompositions occurred at 400 and 430 °C, respectively, for PMMA and PCL, meaning PMMA degrade faster by a temperature of 30 °C.

Constructive combination of naturally derived materials with different synthetic nanomaterials like a carbon nanotube, graphene, mineral and metallic nanoparticles are of immense importance to material scientists and engineers. The superior properties of the novel materials make them a good candidate for high-temperature applications, electrical and thermal conductivity, gas barrier, complex actuator and optical applications [101]. Unique and effective integration of biopolymers and nanoparticle has contributed significantly to the improvement of thermal properties of polymeric composites. The unusual thermal and electrical conductivities of rare carbon nanotubes have induced and widened the global interest in using nanotubes to enhance the properties of polymeric materials.

Winey et al. [100] reported that the electrical conductivity of carbon nanotube reinforced polymer composites is described by percolation, leading to significant increase in electrical conductivity within the range of 10^{-5}–1 S/cm. The improvement

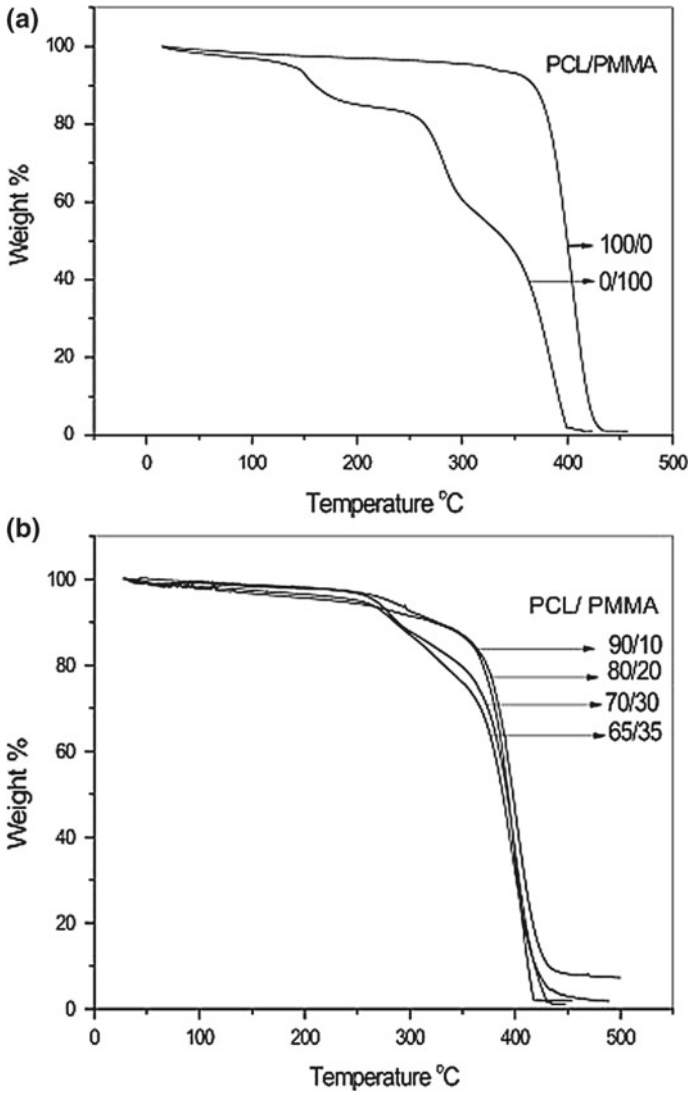

Fig. 10 TGA thermograms of (**a**) pure PCL and pure PMMA (**b**) PCL/PMMA blend films. *Source* [2]

is attributed to the presence of interconnected networks of nanotubes. These networks of nanotubes are also responsible for flame retardant improvement which is achieved by forming a protective layer/shield of nanotube residue.

7 Future Trend in Biopolymer

7.1 Electronic

In the future, global energy demand will be achieved from other sources different from fossil fuels. Fuel cells have been foreseen to play a remarkable role in achieving the expected goal. Fuel cells are recognized as an alternative to the conventional batteries and internal combustion engine generators. The next phase of research is upscaling from the laboratory size to commercial level. Therefore, fuel cells will become a global commodity in the global market. Further modification of the basic properties of biopolymer and nanofiller can contribute significantly to improve its application for electrical components. This has been the trend for decades. Klotzbach et al. [50] prepared biodegradable and biocompatible hydrophobic chitosan membrane by modified chitosan with decanal aldehydes, butanal, hexanal or octanal, which can be used to replace Nafion® for coating electrodes in both fuel cell and sensor applications. Similar observations were reported by Klotzbach et al. [51].

7.2 Biomedical

For vaccine delivery, the utilization of organic–inorganic bionanocomposite is very recent and the field is yet to see significant developments. Some of the nanoparticles, which might be helpful for such applications are calcium phosphate, iron oxide and layered double hydroxides (LDH) [102]. In a test sample, the surface of sepiolite clay was modified with xanthan to deliver influenza vaccine. Further developments in biopolymer reinforced nanoparticles have shown that bionanocomposite-based vaccine delivery system has the potentials to offer the thermal stability of vaccines, which is a crucial and important consideration for stocking of pre-pandemic vaccines [17]. There is an upcoming development of unique bionanocomposites materials, introducing multifunctionality; this is a promising research area that takes advantage of the synergistic assembling of the biopolymers with inorganic nano-sized solids [79]. Advances in the areas of biopolymer will facilitate the advancement of new generations of biopolymer-based materials with controlled function, offering extended application in the area of biomedical. Recent progress in technology and knowledge growth in bioengineering, biochemistry and molecular biology have added to optimizing the biological performance of biopolymer-based formulations and the areas for emerging applications [23]. There is an ongoing

research on biodegradable metal contacts as bioresorbable metals for cardiovascular and orthopedic applications [27, 54].

7.3 Packaging Material

Prediction of the exert date and time and possible shelf life of packaged food and the packaged material can be accurate to a greater percentage with the development of smart packaging material judging from the studies that have already been conducted [104]. Consumers can be better informed about the product they are consuming and ascertain if the product is still good for their consumption and not just judging by the date written on it by the manufacturers which could be misleading sometime. Further research on the improvement of biopolymer and the filler nanoparticles will ensure the realization of the healthy packaged food and extended shelf life for both the packed food and the packaging materials.

8 Conclusion

The chapter presented the development of composites and nanocomposites from biodegradable resources such as plant and animal based. It is observed that these materials on their own do not possess the required properties, therefore, the need for reinforcing it with fibers and nanoparticles. Other ways of enhancing the properties include polymer blend, the addition of coupling agent and occasionally, heat treatment. Various types of biopolymers were also discussed. The chapter also highlighted what determines the choice of material in order to enhance the properties. Finally, the chapter concluded by outlining some observable trends in the area of biopolymer-based composites and bionanocomposites for energy, biomedical and packaging applications.

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Chapter 15
Biopolymers and Nanocomposites in Civil Engineering Applications

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1 Introduction

Though there is an increased demand for eco-friendly materials for agricultural, industrial and infrastructural developments, polymer materials used for these purposes are non-degradable and pose environmental threats. Efforts are now being made to utilize bio-based materials to achieve the earlier stated purposes in order to produce sustainable materials that are economical, safe, and environment-friendly [85]. Composite materials are materials resulting from the mixture of at least two,

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unlike constituent materials which are of different forms, insoluble in each other, physically distinct and chemically inhomogeneous [69]. Biopolymers are divisible into two categories, namely the biopolymers derived from living creatures and biopolymers essentially polymerized but biodegradable and derived from renewable resources [14, 157].

Recent advances have shown interest in the replacement of synthetic materials with different types of naturally occurring materials. Scientists have shown attention to natural fibers as a beneficial material to the ecology because there have been several explorations on vegetable-derived cellulose or vegetative cellulose [14]. Cellulose derived from plants has been explored for many decades [23]. At the present time, huge solid of agricultural disposal problems resulting from waste have been generated from the haphazard disposal of heavy quantities of poultry feathers [14].

Keratin fibers are materials suitable for use as high structural reinforcements of polymer-based composites because of the biodegradable eco-friendly, cost-effective, hydrophobic, insoluble in organic solvents, low density, nonabrasive, renewable, and warmth retention properties they possess [110]. Chicken feathers contain 91, 1, and 8% keratin (protein), lipids, and water, respectively [55]. Chicken feathers are mainly made up of cysteine, glycine, proline, and serine and nearly no methionine, lysine, or histidine [145]. The sequence of amino acid CFF is very similar to those of other feathers [78].

The occurrence of oil spillage in many oil-producing countries in the world has led to environmental pollution, environmental disaster and destruction of maritime ecosystem [6, 12, 20, 36, 105, 153]. Environmental tragedies resulting from oil spillages had led to huge losses in the economic and ecosystem services. It had also caused negative impact not only on the economy but also in accidents occurring from oil tankers collision, environmental and human health balances [44, 60, 115, 120, 178].

Recent advancements in nanotechnology are set to enhance the development of new biopolymers and improvement of known biopolymer materials. Studies on cellulose nanocrystals, which have a dimension of at least one of their sizes as 1–100 nm, are making the waves in recent research with the projection of enhancing development or production of sustainable, environment-friendly, and high-performance construction materials [28, 33]. Cellulose is not only the most abundant organic polymer in the universe, but also biodegradable, carbon neutral, and renewable. About 1.5 million tons of cellulose is produced from the global annual biomass [86]. Cellulose could be processed into large or commercial scale at very low cost when compared to other materials. Nanocrystals of cellulose have the potential of providing a green alternative to carbon nanotubes in the area of reinforcing or strengthening materials such as concrete and polymer [86].

Microbial geotechnology is an emerging branch of geotechnical engineering, which involves investigating the effects of microbiological methods on geological materials for engineering purposes. Microbial geotechnology enhances the modification or improvement of the mechanical properties of soil for environmental conservation and construction by means of bioclogging and biocementation [76]. The longevity of ancient structures such as Greek raft and strip foundations, Roman

bridges on the Appian Way, and Egyptian dams and canals proves that geotechnical engineering has advanced all throughout history and ensured the stability of the structures. Subsequently, Coulomb's decisive work on earth pressures done in the 1770s, many works in mechanics and water flow, and similar geotechnical works on effective stress and evaluation of the foundation's bearing capacity and consolidation of soils show modern improvements and developments in geotechnical systems [41, 88, 112, 159–161].

Some ground improvement methods especially concentrate on chemical changes (pozzolanic changes) in the materials of clay soil and its stabilization for civil engineering works. Utilizing biological processes in soils is a recent development in geotechnical engineering. Literature has shown that presence of micro-bacterial in soil resuscitates the biological properties of the soil as it prompts the geotechnical engineers to consider soil as a living ecosystem other than being only an inert material for construction [88]. Biological processes in the soil have the potentials of providing adequate research avenues, possibilities for soil manipulations and simulation [112].

Construction biotechnology is an emerging science-based/technology-based discipline which features deportation of microorganisms and advancement of microbially based materials for the manufacturing of biomaterials for construction. This process has led to the production of cheap, environmentally friendly, and sustainable bio-microbial biogrouts and biocements used for ground improvement construction [154].

The graphene nanoplatelets are ideal reinforcing materials because of their unique electrical, mechanical, and thermal properties. These special properties of graphene have attracted intensive investigations on the possibility of having composites with graphene-polymer. Little work had been reported on the use of graphene for production of cement-based nanocomposites which have multiple functions. It is a challenge to integrate modeling, synthesis, and evaluation of cement as it requires serious works and repetitions for confirmation of the outcomes [7].

A bottom-up approach is employed for the correlation of the atomic assemblage of graphene-cement nanocomposites (GCNCs) in their macroscopic forms in order to adequately evaluate the manufacturing and characterization of the GCNS. The crystallography and chemical composition of the GCNS could be predicted at the atomic level with the use of x-ray diffraction, whereas, at the nanoscale, the chemical and physical properties of GCNC were obtained with the aid of the atomic force microscopy (AFM). There is a strong relationship between the performance and morphology of the GCNCs. Functionalization of the graphene nanoplatelets can improve the overall mechanical properties of the graphene-cement nanocomposites [7].

The use of composites with reinforced fiber polymer for civil engineering infrastructures is on the increase. Fiber-reinforced composites are useful for reinforcing the interior and exterior of concrete, as wraps in seismic retrofitting of columns, in bridge decks and for systems of structural composites. The inherent lightweight and bend-ability of composites aided in their patronage for structural applications. Nevertheless, their general durability, especially under applied load and exposure to unpleasant weather or serious environmental changes, is a cause to worry about [71].

Nanocomposites could reduce the possibility of penetration of corrosive materials into the polymer composites and enhance the improvement of mechanical and thermal properties of composites. Huge amount or combinations of clay and surfactants have been used as curing agents in the production of nanocomposites. The use of any type of nanocomposite acts to either improve or reduce the performance or properties of the base material. This is the reason why one cannot draw a universal conclusion on a nanocomposite like epoxy because its reaction with each material as well as its effects on the mechanical properties varies from one material to the other [71].

For each desired property(ies) sought in civil engineering material, it is important to investigate which of the resins is most compatible in terms of exfoliation of the particles of the nanomaterials or polymers and identify the present applications of such resins or material. The property of the chosen resin or nanomaterial that could improve the civil engineering material must be identified. The production of such a resin or nanocomposite for civil engineering application is feasible. The likely advantage which such polymer or nanocomposite may offer for other existing materials used for civil engineering construction is evident [71].

Polymeric composites used for civil engineering applications must fulfill specific requirements before they are utilized. Standard polymers or additives used for civil engineering applications could create problems in the process of trying to exfoliate nanoparticles. Adhesives and polymer composites fabricated or made on sites should be polymerized either at ambient temperature or marginally higher temperature in the space of minimum period. The fabrication of pre-cast units in the factory or warehouse allows for elevated temperature and increased curing cycles for the exfoliation of nanoparticles to be achieved. Hence, production of parts of nanocomposites by pultrusion is used for the control of the process of exfoliation. Nevertheless, better understanding and mastery of the process can enhance the transfer of the technology for on the site layout techniques [71].

A newly developing area of nanotechnology is the clay nanocomposite materials which has the tendency to produce a list of different benefits to the present matrix polymers. Clay nanocomposite materials are yet to be used. Though clay nanocomposite materials possess the ability to elongate the service life materials located in aggressive environments and could be useful for the improvement of the durability of materials like carbon fiber composites and glass, they are yet to be used or incorporated for the production of any known civil engineering material and construction. The extension of the service life will encourage the use of clay nanocomposite materials, as it would give assurance of obtaining stability and a prolonged durability of material thereby making it appropriate for a wide range of application [71].

The similarity between bone, concrete, and shale is the hydrated nanocomposite structure of their load-bearing phases. However, the connection between the genesis, mechanical properties, and microstructure of the three materials shows mystery which poses great difficulties in differentiating them [165]. Groups of complex chemo-mechanical materials that have heterogeneous variations atomic to macroscopic scales are called hydrated nanocomposites. Examples of hydrated nanocomposites are: calcium–silicate–hydrates (C–S–H) which is the binding phase in the entire cementitious materials, the load-bearing clay fabric obtained from shales, the

sealing layers present in majority of the hydroxyapatite and hydrocarbon reservoirs, and the mineral-binding phase located in the ultrastructural formations of bone. These materials (hydrated nanocomposites) all possess structural water incorporated in sheet-like or plate-like patterns of their atoms at nanoscales. The hydrated or water-faced nanoparticles form the essential building block whose characteristic is to reduce the macroscopic diversities of the material [165].

Statistical analysis of instrumented indentation method is widely adopted for the characterization of the nanomechanical behavior of the C–S–H phases in shales and bones as applicable for the measurement of elastic properties and hardness of heterogeneous materials. The desirability of this method is that the mechanical phases of these hydrated nanocomposites can be obtained in situ through the conduct of large grids of indentations on greatly heterogeneous samples. This has a proper choice of indentation depth in order to ensure self-similar characteristics of classical continuum indentation analysis. The multiscale material phase of hydrated nanocomposites cannot be recapitulated in bulk form, as it is difficult or impracticable to indent on explicit material phase with sufficient repetitions. In the first part of this paper, we also present the latest experimental protocol we developed and validated for different hydrated nanocomposites [165].

The inclusive picture is that hydrated nanocomposites are nanogranular materials with nanomechanical properties gingered by the packing of their elementary particles. By the particle packing, the statistical nano-indentation technique provides a basis to quantitatively assess the nanogranular state of hydrated nanocomposites in their in situ form and determine the mineral compositions and structural anisotropy. C–S–H is the base particulate component of bone and shale with strength behavior that is isotropic in nature. The strength results from cohesive bonds activated at a particle to particle contact surfaces, which are sufficiently smaller than the cohesion within the mineral. The isotopy indicates that the orientation of the contact surfaces is strong but with non-negligible friction as a result of the particle to particle interlock. Friction in deposited clay shows indication of smooth deposition and compaction of clay particles, thereby reducing the particle interlock and increasing the density based on the particle size distribution of the clay [165].

Concrete is a cementitious material, which has its basic properties affected when materials dispensed at the nanoscale are used with it. Cement-based materials are quasi-brittle materials in that they have low tensile strength. The reinforcement of cement- or concrete-based material is done in millimeter scale for macro-fibers and micrometer scale for microfibers. However, nano-sized fibers like carbon nanotubes are reinforced in the nanometer scale. Nanomaterials such as nanotubes have the potential to produce cementitious composites with high performance [144].

Polymer or clay nanocomposites (PCNs) demonstrate some unique characteristics. The PCNs have shown some unique properties when compared with virgin polymers or polymer composites filled with conventional inorganic particles. Addition of small clay quantities to nanocomposites can substantially improve its mechanical properties. It can also result in increased stability and heat distortion temperature, reduced gas or vapor permeability and flammability [64]. Polyacrylamide (PAM) is a soil-stabilizing additive which has been in use for over a decade. It is being used for

erosion control in the course of irrigation [54, 172], to reduce soil and wind erosion at road cuts and construction sites [133] and to achieve rapid formation for landing pads of the helicopter in order to reduce dust clouds when helicopters land especially during military operations. Polyacrylamide (PAM) is also informally called "the class of polyacrylamide homopolymers and their acrylamide/acrylic acid copolymers" [121].

Polyacrylamide is commercially available for water erosion and wind control, typical of an anionic copolymer which has approximately 15–40% acrylamide chain segments exchanged with the acrylic acid group. Therefore, the commercial value of PAM is for stabilizing soils as a polyelectrolytic random copolymer which is bordered by oppositely charged salts in order to prevent anionic charges. The molecular weight of polyacrylamide used for the purposes earlier stated is between 3 and 25 million. However, the commercially available types of PAM have a molecular weight of between 12 and 20 million [121].

A strategic goal with long-term framework is consequently to discover a pathway for the manufacturing so as to fashion a structural mandate for the platelet reinforced composites and imitate mollusk shells-based layered structures for the production of materials for civil engineering applications [77, 170, 186]. Biopolymers are chemicals which have the ability to maintain low toxicity and at the same time preserve themselves. Biopolymers can also be defined as the bricks of living organisms or reconstruction of bones. Biopolymers are substances produced from non-toxic, biodegradable, biocompatible by-products with little effect on the environment [185]. Life cycle analysis is a useful tool for determining the compliances to the issues relating to the safety, economy, and sustainability of the environment. It is used for the assessments, design, monitoring, and improvement of the sustainability of producing biopolymers [150].

Nanocellulose is not only smaller than cellulose but also has diameters smaller than 10 nm, which enhances its uniquely special engineering properties. It has high mechanical properties resulting from its large surface area. Nanocellulose also has low visual scattering lights. It is derived from the disintegration of plant pulp cellulose or by the feat of bacteria of certain types. After the production of nanocellulose, it can be used for the production of see-through films, hydrogels, fibers, and aerogels which have amazing optical, thermal, and mechanical properties. Inorganic nanoparticles (NPs) are carried by the stated substrates thereby enabling the production of nanocomposites which possess properties of the constituent materials [175].

Nanocellulose is biocompatible, biodegradable readily available and economical; hence, it is considered as a sustainable nanomaterial. Intertwining nanocellulose results in porous, bulk material with high strength like films, aerogel, and nanocellulose papers [26, 140, 158]. The porous nanocellulose is used to impregnate a wide range of nanomaterials as substrates. The nanocomposites produced have the advantage of combining the properties of the two nanomaterials and perform the synergized properties. Montmorillonite and calcium carbonate, metals of Ag, Au, Ni, and Pd; $Ca_x(PO4)_y$ mineral; and carbon (carbon graphene and nanotube) nanomaterials were incorporated into substrates of nanocellulose. The products demonstrated excellent catalytic, optical, and electrical properties of the nanocomposites [175].

For over a decade, there has been renewed interest in reinforcing synthetic polymer with fiber fragments and cellulose fibers. Nanowhiskers obtained from plants and nanofibrils obtained from animals had been evaluated for possible reinforcement of synthetic polymers to produce films and lacquer. Addition of varying proportions of cellulose to composites showed the potential of enhancing the strength of synthetic polymers [52]. There are still challenges in producing complete degradable nanocomposites from the utilization of cellulose nanofibrils as reinforcement and biopolymers as a matrix. Permanent coagulation occurs because of the heavy presence of hydroxyl groups at the surface of nanofibrils. As a result, their ability to reinforce nanocomposites is drastically reduced. Appropriate modification of cellulose nanofibrils is required for the marching of the hydrophobic or hydrophilic property of the polymeric matrix [52].

Nanocomposites are engineered structured produced from more than one materials having different chemical and physical properties and having a dimension of at least one of its sides below 100 nm. Wood exemplifies natural nanocomposite because it possesses cellulose fibrils within the matrix of lignin and hemicelluloses. The main constituents of wood that form its structure are cellulose, lignin, and hemicelluloses [52].

Pulping is the process of obtaining cellulose fibers from wood through either chemical or mechanical method. Extraction of cellulose fibers from wood through mechanical method is energy intensive. However, the entire wood material is used. The chemical pulping process produces half of the entire wood while the remaining half is dissolved. Advancements in modern technology have, however, led to the means of effectively recovering chemicals produced from the chemical process and burning the remaining residues. This recovery process shows that the combustion heat covers the entire energy consumed by the pulp mill [48].

Though cellulose is basically derived from wood, it is, however, derivable or obtainable from some vascular plants such as wheat or corn. Cellulose can also be sourced or obtained from different types of algae (*Valonia*, *Oocystis apiculata*), bacteria (*Gluconacetobacter xylinus*), and even tunicates. There could be a great variation in the structures of cellulose because the structure of cellulose depends on its source [52]. The microfibril angles are the characteristic orientations in which the cellulose microfibrils are organized. The organization differs in line with the cell wall layer and plant type. The coordination or alignment of the microfibrils is coordinated or dictated by the microtubules, which could be located parallel to the microfibrils. There is a strong effect on the mechanical properties of fibers in the various plants as a result of the orientation of the microfibrils. Low microfibrils angle, with the almost parallel orientation of the microfibril nearly parallel to the fiber axis, results in high modulus of elasticity while large angles lead to great elongation at break [87].

Fibrillar structure and huge amounts of hydrogen bonds of the cellulose leads to very high tensile strength. The structural element of a plant carries the load in tensile mode [149]. Cellulose microfibrils isolation in the plant was first done in 1983 [73, 163].

2 Characterization of Biopolymers and Nanocomposites

Biopolymers can be characterized based on their sources such as agricultural resources, biotechnology synthesis, and fermented microorganisms [125]. Biopolymers from agricultural sources are alginates, cellulose, chitin, chitosan, polysaccharides, and starch. Biopolymers from synthetic biotechnology are poly-*p*-phenylene, polytrimethylene terephthalate, biopolyethylene (bPE), polybutadiene succinate, and polylactides (PLA), while biopolymers obtained from the fermentation of microorganisms are polyhydroxyalkanoates, e.g., polyhydroxybutyrateonal synthesis [13].

Literature has shown that the atomic structure of cellulose obtained from the models of its crystals possesses stiffness as high as 206 GPa [45]. Literature has also shown that cellulose nanocrystals have specific Young's modulus (ratio of Young's modulus to the density of cellulose crystal) of approximately 85 Jg^{-1}, which is far greater than that of steel that is only 25 Jg^{-1} [46]. The modification of the modulus of elasticity of the cement board with nanocrystalline cellulose has been patented [162]. The sale of nanocellulose in the cement industry is projected as a minimum of 4 million metric tons [37]. Biopolymers such as starch, chitosan, and PLA possess poor mechanical properties as against synthetic polymers that possess great mechanical properties. Hence, cellulose nanofibers are utilized for the reinforcement of nanomaterials; this can aid conversion of biopolymers to biocomposites with improved mechanical strength [86].

Filamentous bacteria of the genera Nocardia, Sphaerotilus, Haliscomenobacter, Microthrix, Beggiatoa, and Thiothrix are commonly used for treatments of wastewater in the aerobic tanks of water treatment plants and could be useful for bio-binding of soil particles [16, 143]. Aerobic bacteria can be applicable for biocementation, bioclogging, and bio-binding soil particles as different species of the aerobic bacteria could produce slime in large quantities, form filaments and chains, increase pH, and oxidize different types of inorganic and organic substances [76]. Grouts are suspensions or solutions of acrylamides, acrylates, polyurethanes, and sodium silicate or water-insoluble gel-forming biopolymers of microbial origin produced in the industry, such as: chitosan, xanthan, polyglutamic acid, polyhydroxybutyrate, and sodium alginate used as grouts for soil erosion control, mitigating soil liquefaction, and enclosing of bioremediation zone [50, 61, 76].

The impact of multiscale research at the nanoscale could resolve the three-dimensional packing of the phases of hydrated cement and their behaviors with nanoparticles. Adding nanoparticles to cement could enhance both the microscale and nanoscale structure of the cement. Though literature has reported, the behavior of cement with the addition of common nanomaterials like carbon nanotubes and nanofibers, the behavior of cement with the addition of functionalized and exfoliated graphene nanoplatelets has not been well reported [7]. It is therefore important to investigate the mechanical, physical, and thermal properties of GCNCs. There is a possibility that addition of small amount of graphene nanoplatelets to cement could greatly improve the impact strength, flexural strength, and tensile strength of composite materials thereby improving their toughness [7].

The pull-out MD simulation can be used to determine the effects of graphene on cement and cement composites. Embedding graphene nanoplatelets in the C–S–H phases of cement could broaden the knowledge on the improvement of the cement properties with the addition of graphene. This will also give clues on the adhesion and interfacial failure mode required to determine the optimum nano-reinforced cement characteristics [7].

Polyvinyl chloride (PVC) is an important thermoplastic material which has been used for fabrication of wire cable insulation, pipes, and window profiles due to its durable nature and valuable properties such as super physical and mechanical properties, high abrasion, and chemical resistance [109, 171]. Conversely, when PVC is polymerization, many isomeric forms occur and structural defects happen from the main chain. These irregular structures can lead to induction of thermal instability of the PVC in the process of the polymer usage, owing to the fact that thermal dehydrochlorination of the PVC frequently starts with internal allylic chloride and defects in the structure of tertiary chloride in the main chain [171].

Industrial research has led to the emergence of a new group of a material called clay–polymer nanocomposites which are produced from little addition of clay into polymer matrix causing dramatic enhancement of the mechanical and barrier properties. A material such as a nacre, which occurs in nature, is a blend of a vast content of strong and tough polymer platelets with layered structure with a strength of between 4 and 10 MPa $m^{1/2}$, although the reinforcement may be approximately 1 MPa $m^{1/2}$ if the material is brittle. Nature has aided the synthesis of materials such as smectite clay tactoids to imitate the structure of nacre with the use of high aspect ratio reinforcements with a high modulus of elasticity [186].

The technologies for processing chicken feather fiber (CFF) had been developing, and the particulate (quill) fractions have been processed and patented in the USA [3, 145]. Chicken feather fiber has been evaluated for its suitability as a reinforcing element in cement-bonded composites by [3]. The study examined the use of CFF waste in the form of barbs and rachis. Boards which contained 5 and 10% fiber and/or ground feather by weight of cement produced comparable strength and dimensional stability to composites made from commercial wood fiber-cement of similar thickness and density. The study revealed that the more the fiber content in the cement-based composites, the higher the susceptibility of the cement-based composites to water absorption and thickness swelling especially after 24 h of soaking in water. The modulus of elasticity and modulus of rupture also reduced. A waste CFF content of 10% feather content was recommended as a replacement in the cement-based composite [22].

Besides, recent advances suggest that nanocellulose could serve an as hard template for synthesizing new nanomaterials [108, 146]. The identified forms of nanocellulose are: homogenized cellulose pulps which are also called nanofibrillated cellulose (NFC) or microfibrillated cellulose (MFC); acid-hydrolyzed cellulose whiskers which are also called cellulose nanocrystal (CNC) or nanocrystalline cellulose (NCC); and cellulose produced from bacterial or bacterial cellulose (BC) [148]. Figure 1 exemplifies the connections between the different groups of the

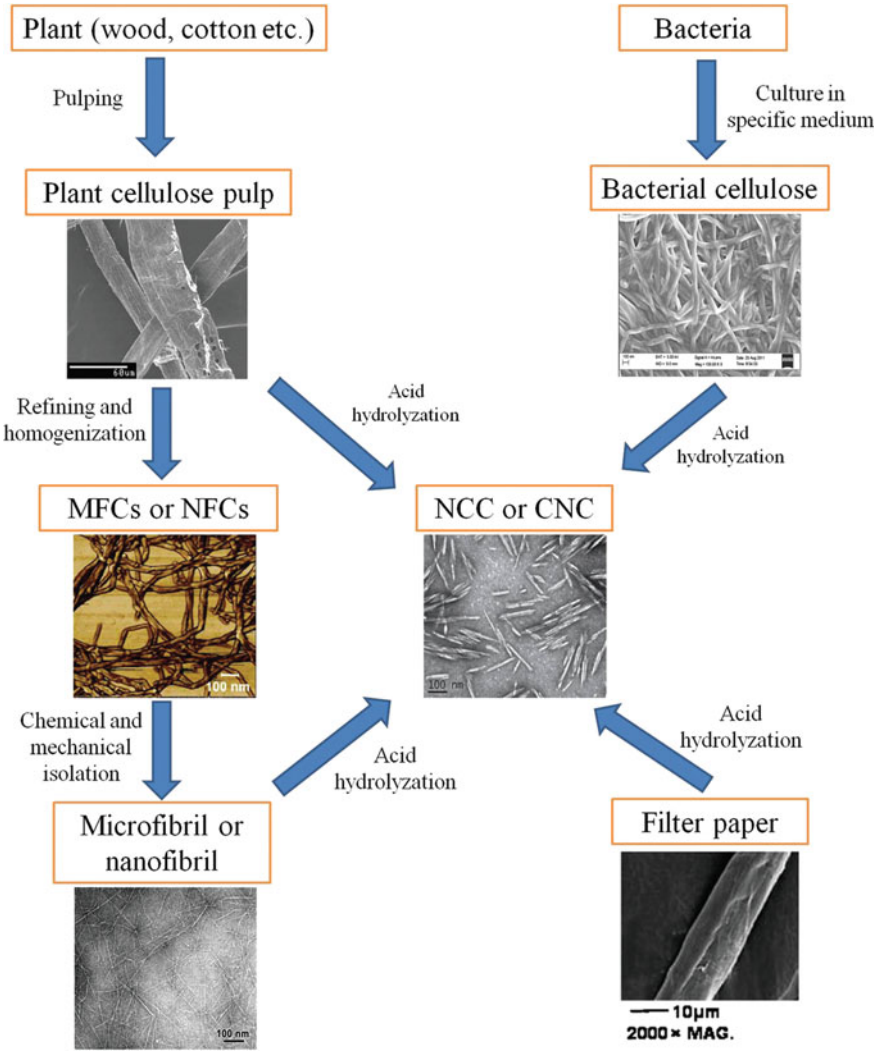

Fig. 1 Connections between the different groups of nanocellulose [175]

aforementioned nanocellulose groups. Microfibrillated cellulose contains parcels of microfibrils which are actually primary components of the parent cellulose [175].

3 Use of Biopolymers and Nanocomposites for Civil Engineering Infrastructures

Cheap materials are created to enhance regular transfer of silver ions in water to produce drinkable water free from microbial. The effect of combining different nanocomposites to salvage poisonous water contents or contaminants like lead and arsenic could aid affordable yet purified portable water without the use of electricity [138].

Albert [5] stated that biopolymers have been utilized for construction purposes for centuries. He added that the use of vegetable fat and bio-based admixtures to produce air lime mortar was dated back to the Roman Empire. Bio-admixtures were used by the Roman Empire to modify construction materials. Proteins, which are biopolymers, were used as retarders for the setting of gypsum while an air-entraining agent was derived from dried blood [129]. Chinese utilized fish oil, egg white, and blood-based mortars, which were impervious, in the construction of the Great Wall [181]. The use of small contents of vegetable oil with lime for production of mortar for construction of the Portuguese fortress was dated back to 1507. Mortar referred to in the previous statement was described as an excellent and greatly durable material beyond stones by a British Naval Lieutenant, A. W. Stiffe, over 300 years after the fortress was built [126, 135].

In the 1920s, lignosulfonate, a biopolymer admixture, was used for the plasticization of ordinary portland cement (OPC) concrete in large-scale construction works [130]. The OPC is the most patronized civil engineering construction material across the globe. Its production [127] is approximately 10,000 million tons annually, and it is envisaged that it can increase by 100% by the year 2053.

Close to 15% OPC concrete produced is modified with chemical additives, in either fresh state or hardened state. Condensates, naphthalene, melamine, and polycarboxylate copolymers are the synthetic polymers used for the production of concrete plasticizers in order to modify the durability, workability, and strength of concrete. Chitosan, lignosulfonate, pine root extract, protein hydrolysates, and vegetable oils are typical biopolymers used in concrete. Polyfurfuryl alcohol bioresins are agricultural wastes which show great potential for use in engineering structures [63].

Biopolymers are greatly used in the construction industry. In the year 2000, the sale of biopolymers was estimated at $2 billion and an increase in the sale was projected for the subsequent years. Majority of the biopolymers in the construction industry were consumed by dry mix mortars and OPC, whereas over 500 bio-admixtures are recently been used by industries producing building materials [130].

The population of the urban cities in the world was projected to increase from 3.4 to 6.4 billion people between the years 2009 and 2050. The construction industry is set for an astronomical growth to accommodate the population of people in the urban cities of the world [40]. A study by Seto et al. [142] estimated the land expansion by the year 2030 as 1.2 million km^2. Consequently, there will be great demand for the use of biopolymer-based materials for civil engineering constructions [9]. Cellulose can be used as aerogel (cellulose aerogel) for building materials because

of its high-performance thermal insulating properties [31, 58, 118]. It also possesses fire retardant properties [177].

Thermal insulators with high-performance properties are materials that possess thermal conductivity less than 0.020 W/(m K) while current insulator (petroleum-based) materials such as extruded polystyrene (XPS) and expanded polystyrene (EPS) possess a thermal conductivity of about $0.03e^{0.06}$ W/(m K). Thermal conductivity is a very important means of classifying materials because thermally insulating materials are used for effectively reducing heat losses in buildings, thereby increasing their energy efficiency. It is important to note that building industry consumes the greatest energy in line with European Union (EU)'s overall final energy consumption [97].

The Energy Road Map 2050 given by the European Commission [51] stated that higher energy efficiency in existing and new buildings is critical or important for the revolution of the European Union's energy system. This is emphasized in the European Energy Performance of Buildings Directive (EPBD), 2002/91/ EC and recast as a directive in 2010/31/EU by the European Parliament on May 19, 2010. A new perspective to the EPBD is the institution of the theory of nearly zero-energy building [123]. A special funding was awarded to building energy efficiency under an EU framework program called HORIZON 2020 [122].

A report by the Navigant Research [116] projected that the European market for building energy products and services would be 80 billion euro by 2023. Current insulators such as EPS and XPS release toxic fumes when burning but aerogel is non-inflammable [124]. The nonflammable properties of the aerogel give it an advantage over the EPS and XPS. Some literature on biopolymers and bio-based admixtures did not discuss their applications to construction materials. Some literature, however, discussed biopolymers and bio-based admixtures for plasters and cement only [125].

Glass fiber-reinforced polymer (GFRP) composites have been used for fabrication of load-bearing materials with pultruded profiles for civil and structural engineering applications such as buildings and bridges [35]. The pultruded GFRP has been used to build bridges and decks for road bridges. The GFRP composites are also used for constructing buildings in aggressive and corrosive environments such as swimming pools, cooling towers, and wastewater treatments. GFRP composites have a low weight which could make it useful for renovation or repair works in buildings. However, efforts to utilize GFRP composites for construction of residential and office buildings have not been successful [35]. A diagrammatic representation of the GFRP profile and bridge is presented in Fig. 2.

GFRP composites have been used for the construction of tall buildings. The low weight of the GFRP composites enhances or aids its suitability for the construction of the tallest building shown in Fig. 3, which could be detached, dismantled, and re-assembled. Limitation of GFRP profile to building construction is due to its low thermal conductivity. The materials are also susceptible to an elevated temperature as they are not fire resistant. The room condition, as well as the conditions in the buildings, is not such as those of the bridge or outdoor structures that are designed and built with provision for heat escape and fire resistance [35].

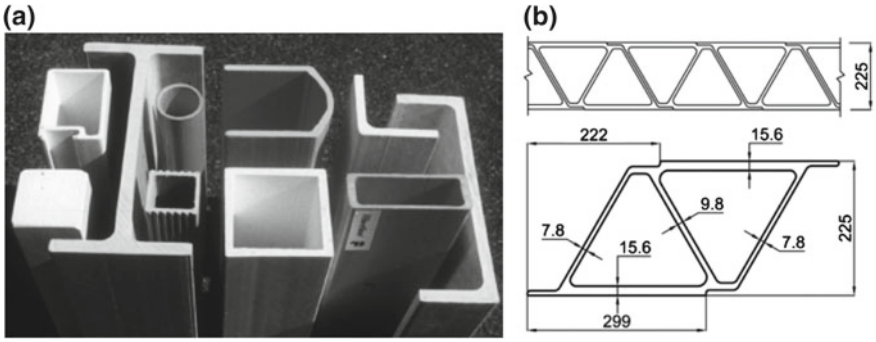

Fig. 2 Typical pultruded GFRP profiles (left) and pultruded GFRP bridge deck system with triangular cell configuration (right) [35]

Fig. 3 Eyecatcher building, Basel, 1998: three load-bearing frames, bolted joints [35]

The process suitable for fluid grouts filling of soil whereby water flow is being controlled is microbial grouting in situ whereas the process whereby soil voids are filled with fluid groups in order to control water flow is a process called chemical grouting [81]. Bioclogging entails filling pores in soil or other materials with microbial in order to reduce its hydraulic conductivity and porosity. Biocementation is the use of microbial processes, in in situ form, to produce particle-binding materials for the improvement of the shear strength of soil. Microbial Geotechnology is complex as it requires the synchronization of knowledge in ecology, geotechnical engineer-

ing, geochemistry, and microbiology. The microaerophilic and facultative anaerobic bacteria are the most applicable microorganisms in soil bioclogging or biocementation. Nevertheless, anaerobic respiring, anaerobic fermenting, and obligate aerobic bacteria may be considered for applications in geotechnical engineering [76].

Suitable microorganisms can be used for soil modification, erosion prevention, or land reclamation through biosynthesis of extracellular biopolymers and by microbial growth [76]. Biogeotechnology is a division in geotechnical engineering which deals with the use of biological methods to solve problems in geotechnical engineering. Nowadays, biogeotechnology entails the applications of plants or vegetative soil cover for control of soil erosion, protection of slope, slope failure prevention, and reduction of water infiltration unto slopes. Advantages of biogeotechnology are a low investment, low maintenance costs, environmental preservation, and achievement of good aesthetics [81].

Biopolymers have been evaluated for in situ and ex situ applications with the aim of improving the engineering properties of soil. Addition of biopolymers to soil has proved to improve the shear strength but reduced the hydraulic conductivity of the soil [83, 119]. Martinez et al. [107] showed that addition of 0.3% xanthan gum (a biopolymer available in commercial quantity) to silt could reduce the hydraulic conductivity of the silt by two orders of magnitude (to the tune of 10^{-6} cm/s) and increase the shear strength by about 30%. The reduction in hydraulic conductivity of soil could be as a result of soil grading and the hydraulic gradient applied [43].

Biopolymers are used for biodegradable drilling of boreholes because they possess bioplugging tendency [72]. Biopolymers are useful for temporary excavation support fluids in order to create permeable reactive barriers for groundwater correction. The permeability of sand can reduce under two weeks when the sand is modified with biopolymer slurry [84]. Attempts to improve the in situ shear strength of sand show that in situ biopolymer growth and extracellular polymeric substances (EPS) could form hydraulic barriers thereby reducing the hydraulic conductivity of sand [21, 25, 141, 179]. Literature has shown that clogging of filters in landfills, dams, and water treatment plants resulted in the growth of biofilms [38, 76]. An investigation conducted in October 1985 on the subsurface drain clogging at Ergo Tailings Dam (ETD), Republic of South Africa, showed that growth of arsenic-resistant microorganisms occurred and the growth caused clogging of the geotextile drain filter [98].

Polysaccharides of microbials can be used as cement admixtures. Biodegradable microbial bioplastics are utilized for temporary constructions. Biotechnologically produced bioagents used in construction can be pure or enrichment cultures of activated indigenous microorganisms or microorganisms of soil. Biotechnology is applied in the construction world in the bioclogging, biodesaturation, biocementation, and bioaggregation of soil. Construction materials produced biotechnologically as well as microbial-based construction technologies are advantageous over conventional construction materials and methods. A thorough evaluation of the processes of biotechnology constructions would lead to great economic benefits and environmental sustainability [154].

A number of million tons of sewage sludge are generated from municipal wastewater treatment plants (MWWTPs) annually. Malliou et al. [106] stated that the addition

of between 0.30 and 0.39 dry sewage sludge to cement would be of economic benefit to utilize harmful sludge which embodies large quantities of heavy metal organics and microbial pathogens. Records have shown that dry or raw sewage sludge from MWWTPs could be used in place of filler in bituminous and concrete mixes and could be used for the construction of landfills [29, 56, 82, 100, 134, 152, 182].

The system or method of determining faults and their locations within structures is called the structural health monitoring (SHM) that is vital for the sustainability and management of huge and multi-story buildings as well as heavy infrastructures [92, 93]. The lifespan of buildings and other structures is limited or reduced as a result of failures on the structures due to excessive usage and inadequate maintenance [80, 101]. America has a large record of bridges which require repair because the bridges are either old or under-maintained. A total sum of 2 trillion USD was estimated for the repairs of such bridges and large-scale infrastructures [131, 176]. Health and safety of civil engineering infrastructures could be achieved by interventions such as regular maintenance and timely inspection of infrastructures, thereby ensuring their sustainability [24].

Though damage detection techniques such as pulse-echo, non-destructive, acoustic emission, and dynamic response exist, detecting damages or failures in large-scale infrastructures is very complex, infeasible, and very expensive. However, a cost-effective way of detecting the failures or damages in such large structures is by utilizing sensing skin that consists of soft elastomeric capacitors arranged in matrix format over the entire infrastructure. This method is mainly for detecting changes in strain over a large area without altering the integrity of the structures using the SHM system [92, 93]. The method is comparable with biological skin as changes at a point could be monitored over the entire surface [103].

The robust capacitive-based sensor is a sensing skin which houses numerous individual capacitive sensors known as sensing patches with each having its own shaped areas. Each sensing patch is made from a soft incompressible polymeric membrane enclosed by extremely compliant and stretchable electrodes forming the stretchable capacitor [103]. The capacitance (C) of the sensing patch is dependent on the surface area (A) with thickness (d), vacuum permittivity ($\mathfrak{E}_o$), and permittivity of the polymer ($\mathfrak{E}_m$). Therefore, the capacitance can be represented with Eq. (1):

$$c = \varepsilon_o \varepsilon_{mA}/d \tag{1}$$

In the last few decades, the desire for materials with high performance had resulted in the swift development of new sets of materials. The visionary Feynman has revolutionized the nanotechnology world thereby leading to the capacity to create and evaluate materials at a molecular level that is “the essence of nanotechnology”. By this development, the molecular organization has aided in the generation or developments of heavy structures from atom to atom level. The applications of nanotechnology have led to many developments. The world of high-tech has witnessed huge transformations from the utilization of nanomaterials such as nanofibers, nanotubes,

nanowires, and quantum dots for the production of energy, biomedical, environment and electronic equipment, and appliances [7].

Civil engineering infrastructures such as bridges, buildings, and dams are huge and very expensive. In the world of concrete, the constituent materials, which have macrostructures, can be studied and manipulated with nanomaterials in their manufacturing or construction process to produce improved concrete. The cement constituent in concrete has a calcium–silicate–hydrate (C–S–H) dense packing at the nanoscale. Addition of small amount of nanomaterial could greatly enhance the concrete properties. A multiscale evaluation may be required to determine the effect of the addition of nanomaterial to cement in order to evaluate [7, 168].

Uniform dispersion of carbon nanotubes (CNTs) within the cementitious material matrix enhances good reinforcement of the cementitious material. However, nonuniform incorporation of CNTs within the cementitious material results in poor dispersion of the CNTs. Since small amounts of between 0.5 and 2% CNTs initially effectively dispersed into cementitious materials, the CNTs can then be dispersed in liquid form [144].

CNTs showed great potential for improving Young's modulus of cement paste when compared with plain cement paste without CNT's reinforcements. The experiment showed that reinforcement of cement specimens with short CNTs of ~0.08% by weight of cement and that reinforced with long CNTs of 0.048% by weight of cement had shown equal mechanical properties. Nanocomposites reinforced with CNTs possess excellent Young's modulus and mechanical properties [144].

The measurements of the slenderness and particle size of aggregate order than the grain size distribution are its specific surface. The specific surface of the dry condition of the soil can be measured by gas adsorption while that of the soil in aqueous suspension can be measured by selective molecular adsorption. The procedure used to measure the specific surface has a substantial effect on the measured value. The total surface in a soil mass decides the balance that exists in-between the surface-related forces and gravimetric–skeletal forces upon the soil particles. It affects the formation, energy coupling mechanisms, determines conduction, and controls both the sorption and retardation of the chemical reaction [139].

The forces determining the behavior of fine-grained soils are different from those of coarse-grained soils. Skeletal and self-weight forces significantly affect coarse grain soils. As the particle sizes of coarse grain soils decrease, the electrical and capillary forces acting on the coarse grain soils and the specific surface increase. The specific surface (Ss) of a particle of a soil can be defined as the ratio of the soil's surface area (As) to the soil's mass (M). The significance of the soil's specific surface to its behavior can be determined by making a comparison between the magnitudes of the electrical inter-particle forces (Felec) of the soil to the weight (W) of a particle [139].

Degradation results in impairment of the mechanical properties and the process of the PVC. Hence, knowledge of the abnormal thermal stability is imperative to PVC users. Researches on nanocomposites of clay/polymer deal with novel methods for the preparation of high-performance PVC composites. Nonetheless, investigation of PVC has not been given desired or adequate attention. Hitherto, there are

very few literatures on PVC/clay nanocomposites, and one can rarely obtain any literature on the fine structure of nanocomposites when explored [173]. The average molecular weight of PVC was nearly not affected by the presence of organophilic montmorillonite (MMT), and an almost exfoliated nanostructure was obtained [173]. Thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) was used to characterize the thermal properties of in situ nanocomposites by examining the effects of organophilic montmorillonite on thermal stability of the PVC and the likely mechanism that took place. The results showed that nanocomposites show higher glass transition when compared with unadulterated or plain PVC. There was an enhancement of quickest decomposition temperature and reduction in maximum decomposition rate at the outset of the decomposition temperature when OMMT was added to PVC. Addition of nanocomposites improved the thermal stability of the matrix and the formation of residue. A more carbonaceous MMT with compact char structure was formed in the nanostructure surface which prevented thermal degradation of polymer matrix at elevated temperature [64].

Orts et al. [121] stated that polyacrylamide (PAM) has been used for run-off protection and erosion control in approximately 500,000 ha. of land in the USA, Australia, and many parts of the world. Where fine soil, fine sediments, or polluted soil is encountered in the construction of roads, drainages, dams, or external work of buildings, the use of PAM will be very appropriate for stabilizing the soil in order to attain a structurally stable pavement (or road courses).

The military operations and applications of PAM may be out of reach of the general public; however, a large number of important soil applications of PAM have been done for military operations such as their training grounds, sports complexes, and for foundation works for their residential buildings, children schools, and for helicopter landing pads. The reason for a search for an alternative to PAM for agricultural purposes is traceable to increasing market pull-out of organic farming techniques in as much as PAM is not applicable for organic farming [121].

Biopolymer as alternatives to PAM will grow rapidly due to the fact that it will have a marketing edge over PAM as the public perceives biopolymers are comparatively safer natural compounds. Interest in development of biopolymer alternatives for PAM may increase *due* to *economic* drivers. Owing to the increase in prices of natural gas and acrylamide products such as feedstock, the industry may likely align with the use of polymers as an alternative [121].

About 22.5 kg ha^{-2} of PAM is used for the construction of road cuts and stabilization of pavement layers; this is more than tenfolds of the quantity used for irrigation control. The sediment run-off is reduced by 60–85% by application of PAM for erosion control against heavy rains. Acid-hydrolyzed cellulose microfibrils, a biodegradable substitute for PAM, show less effectiveness to PAM of similar concentration but show potential for applicability. The sediments from run-off can be reduced by only using about 80% concentration of PAM [121].

Ash et al. [8] indicated that the most dramatic improvement in the nanocomposite's modulus of elasticity takes place at a temperature range beyond the temperature of glass transition (T_g). The improvement is extremely greater than that of T_g (about 4,000% higher). The heat distortion temperature (HDT) of polymeric materials can

be defined as the heat resistance index of nanocomposites to an applied load [132]. Literature shows that HDT is a function of clay content in line with the ASTM D648-06 [11] specifications. Polymeric materials require that the HDT is increased because clay dispersion is essential for improving polymeric material and because the attainment of such heat distortion temperature is very hard by either conventional filler or chemical modification [57].

For the field coating systems, Fischer [53] stated that the permeability of nanocomposites coatings for water vapor significantly reduced with regard to non-modified coating. The reduction of the permeability of water vapor by a factor of 15 indicates the presence of a strong bond between the methylene blue and clay platelets. Homogeneous dispersion of clay particles in the coating matrix produces a completely transparent coating [57].

Montmorillonite, an outstanding exfoliated clay, was incorporated in polyamides to produce the first polymer clay nanocomposites at the Toyota Motor Corporation in 1985. The nanocomposites produced showed substantial improvement in modulus and strength. Further works have followed from both the academia and industry. A class of recent materials with the least lead time was used for the production of timing belt covers of automobiles just under four years of the discovery of the polymer clay nanocomposites [186].

The greatest role that an engineering material can offer is to be given the confidence to function as a structural element or fabrication material of an aircraft. The Boeing 787 shown in Fig. 4 contains about 50% composite material, mainly reinforced with carbon fiber for the structural components of the airframe. The Royal Aircraft Establishment in Farnborough, UK, was the first to produce carbon fiber composites in 1963. Another important advance in the transportation engineering sector is the recent processing of natural plant oil for the production of polymers which can be incorporated into composites used for producing vehicles. A car model with its body structure fabricated with a polymer derived from soy and reinforced by steel tube was made by Ford in 1940 and patented [186].

Due to the cheap, huge mass-specific properties, low density, and renewability of natural cellulose fibers like wood, ramie, hemp, and flax, they have been acknowledged as beautiful fillers for composites. Embedment of natural cellulose fiber in thermoplastic polymers in a modular ratio of 2:1 is being evaluated for the realization of short fiber-reinforced composites. Advances in the transportation engineering field have led to the production of body panel for a car prototype named “Eco-Elise” which has a solar panel on its roof for powering the vehicle. The Eco-Elise has its body panel made from the composite reinforcement of hemp [186].

Uzun et al. [167] asserted that the impact strength of the CFF-reinforced composites is considerably higher than that of the control composites. Nonetheless, there were insignificant outputs observed for the tensile strength and flexural strength of the CFF-reinforced composites when compared with the control composites. Another study concluded that the chicken feather fiber (CFF) could be used as a reinforcement that could improve the impact strength of the composite [4]. Uzun et al. [167] suggested that CFF could be used as a matrix component in the manufacturing of composites with high specific strength, and this could lead to utilization or reuse of

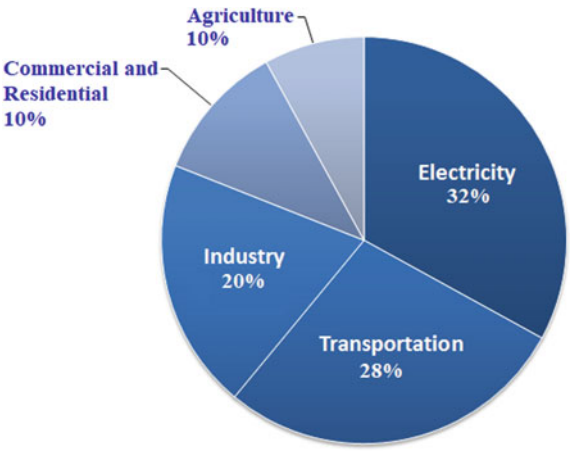

Fig. 4 United States 2012 overall greenhouse gases emission. Adapted from sources of greenhouse gas emissions [166]

large quantities of waste. The use of CFF with other reinforcing materials could be at a very low cost and with the advantage of producing high strength composite in the design and construction/fabrication processes. Barone and Schmidt [15] considered the reinforcement of polyethylene with a chicken feather (CF) with the deployment of bra bender mixing technique. The study revealed that the mechanical properties of the CF-reinforced polyethylene were comparable to the theoretical outputs and complied with the simple composite micro-mechanical model by Uzun et al. [167].

Subramani et al. [155] explored the mechanical properties of composites of polyester and phenyl-ester reinforced with CFF and compared the effects of with or without CFF on the composites. A similar study revealed that the compressive strength of CFF-based composite was enhanced when compared with that of the controls composite. Hence, CFF could be used for many structural and other engineering applications as the mechanical properties of the CFF-reinforced composites improved [17].

CFF possesses good fibrous nature. The morphology of CFF shows very good and the uniform dispersion. By a systematic orientation of the fibers rather than sizing or random manipulation and by matrix-oriented mixing of the fiber while casting, the characteristics of the composites reinforced with CFF would be improved at a cost-effective rate. If fiber orientation is made systematic instead of random and sizing is manipulated also if the mixing technique of fiber with matrix during casting is improved, then an enhanced characterization of the developed composite can be achieved with many cost-effective applications [14].

Clay soil has a wide range of applications in geotechnical engineering. It has been used for dams, nuclear plants, and landfills. The clayey soil has the characteristics of gradually changing its geotechnical properties such as compressibility, shear strength, and swelling when there is an interaction between it and water. There is, however, a remarkable improvement in the geotechnical properties of the clay nanocomposites when compared with natural clay and hydrophobic clay [91]. Clay

Table 1 Chemical composition of clay

Chemical composition	Clay (%)
Al_2O_3	12.22
CaO	11.14
Fe_2O_3	9.88
K_2O	1.23
MgO	8.10
Na_2O	0.2
SiO_2	41.48
TiO_2	0.53
LOI	13

minerals are particulate, very small, and electrochemically active. The engineering properties of a soil mass can be significantly affected by the presence of a small quantity of clay in the soil [74]. In addition to the use of clayey soils for the construction of dams, landfills, and nuclear plants, clay minerals, particularly smectites, can greatly be affected by water presence. Variation in the water content of the clayey soil increases its plasticity thereby reflecting in the soils Atterberg limits. Due to the fineness of the clay minerals, it has very large specific surfaces and rapid ion exchange capacities [27, 91].

Due to the increase in swelling and settlement of clay soil, it is susceptible to volume changes which could affect its stability. In order to eradicate the negative impact that could take a toll on the stability of clayey soil, chemical stabilization is done to reinvigorate the clayey soil and improve its engineering properties [95, 164, 169, 187]. Polymer-clay nanocomposites are a group of materials which have their polymer matrix reinforced by inorganic particles which are uniformly dispersed and having at least one of their dimensions in nanometer [96]. The preparation of clay nanocomposites is by incorporating finely dispersed silicate-layered materials into the polymer matrix. Recent advances in materials have ventured on the polymer or layered silicate nanocomposites [91], which have benefited more than conventional construction materials. Biopolymers are polymers that occur in nature; they are found in living organisms. Biopolymer-clay nanocomposites are polymers that are naturally occurring with the potentials of improved mechanical properties. They are renewable materials, which are biodegradable and are components, which are neither toxic nor noxious components [34, 174]. The chemical composition of a typical clay sample is presented in Table 1.

There is a reduction in the unconfined compressive strength (UCS) of clay nanocomposites compared with that of hydrophobic organo-clay and natural clay. The inference was that clay nanocomposites contain more water than the others as a result of its increased contact angles [91]. This is in consonance with an earlier work by Kurt and Akbulut [90], which showed that the swelling pressures of both clay nanocomposite samples without rubber powder additive (CNC) and clay nanocomposite samples with rubber powder additive (CNCR) reduced when compared with

those of hydrophobic organo-clay and natural clay. In the same vein, the void ratio of clay nanocomposites is greater than that of hydrophobic organo-clay and natural clay whereas the specific gravity of clay nanocomposites is lesser than that of hydrophobic organo-clay and natural clay. Therefore, the clay nanocomposites have more porous structure than natural clay and hydrophobic organo-clay. The unconfined compressive strength suggests that clay nanocomposites have stiff consistencies. Hence, clay nanocomposites are suitable for use as a liner for waste disposal in dams and landfills.

The role of civil engineering staff who specialize in waste management and environmental engineering includes prevention of waste generation instead of cleaning or treatment. Synthetic materials devoid of substances toxic to the environment or the human health should be designed, generated, or used. Design of chemical products should be done with the aim of preservation of their efficacies and reduce toxics. As much as possible, auxiliary substances such as separation agents, reagents, and solvents should be avoided. Where the auxiliary materials must be used, they must be harmless. Where synthetic methods are used for fabrication or production, or in any process, it must be ensured that they must be handled or piloted at ambient temperature and pressure [185].

Knowledge of energy requirements is vital for the assessments and minimization of economic and environmental impacts. All raw materials used must be economic, renewable and not contribute to depletion of the environment. The modification of the physical or chemical processes of material should be avoided as much as possible. Where necessary, the choice of catalytic reagents should be recommended and made over stoichiometric reagents [185].

The design process of chemical products used in the environment must be such that their end function will not be retained to result in products that have harmful degradation on the environment. There must be a developed analytical technology to permit the monitoring of real-time in-process and control before the production of lethal substances. The substances used in chemical processes and their forms should be such that would minimize the possibility of accidence occurrence [185].

Every aspect of the cycle of ammunitions has an impact on human health and the natural environment. It is therefore imperative to assess the hazards that result from health, environment, and occupation. Hence, non-toxic biopolymers are deployed for use in the environment with due considerations on the impact of such material on human health and environment. The military, safety, and health officials are trained to prevent pollution and accidents at work and safe application of biopolymers. The recognition and enhancement of environmental protection are proactive means of maintaining healthy environment order than dogmatic compliance to military rules and regulations [185].

Dispersion of by-products, energetic and explosive materials do exist in the military environment. As a result, it is inevitable to make findings and testing to determine the soil groundwater and its contamination level of the testing area, production sites, and military training grounds in order to maintain a stable, sustainable, and eco-friendly environment devoid of contaminants, pollutants, and toxics. In the army, environmentally friendly activities are encouraged as the environment must be preserved from the chemical, toxicological, and physical properties of the energetic

materials used [185]. The requirements for the use of primary feedstock as a renewable material for manufacturing would increase in order to enhance the achievement of environmental and economic sustainability. For safe, efficient, and effective recycling of ammunitions, recyclable ammunitions must be available and utilized. As a result, biopolymers stand out as a potential alternative to the obsolete energetic materials used. The implementation of biopolymer-based ammunitions would not only be economical, safe, and environment-friendly but also sustainable [185].

Nanocellulose-based nanocomposites show developments which are potentials such as antimicrobial and catalytic activities applicable for water purification. AuNP impregnated nanocellulose with increased loading and size showed great potential as SERS substrate. Nanocellulose also shows potential as a new substrate for fuel cell fabrication and promising energy applications. Ultracin nanofibers with diameters of 2–5 nm can be produced from disintegration of cellulose pulp in the top to bottom arrangement. The ultracin nanofibers produced show potential of astonishing mechanical, thermal, and optical properties. The fiber, film, aerogel, and paper synthesized with the bottom to top arrangement of nanocellulose provided sufficient space to act as a strong carrier for incorporating guest nanomaterials [175].

The exponential rate at which the world is developing has led to increased mass production and global commerce thereby causing depletion of the natural resources. The effect of greenhouse gases (GHG) has resulted into a diminution of the ozone layer and global warning which cause natural disaster overseas. Transportation of people, goods, and service from one place to another is essential for humans to complete their daily events. Vehicle exhausts lead to the emission of greenhouse gases (GHG) and result in environmental pollution. Vehicle exhaust does not only take a toll on the environment but also leads to the development of carbon dioxide (CO_2) gasses in the processes of construction of transportation facilities. Figure 4 presents the summary of 2012 GHG emission in the USA. The data presented on the pie chart show that the contribution of the transportation sector to the GHG emission is above 25% of the 6,526 million metric tons of CO_2 which was the entire GHG emitted [166]. As a result, it is important to evaluate materials such as biopolymers and nanocomposites for the construction of transportation facilities in order to reduce the GHG generated in the environment.

Figure 5 presents a graph showing the cumulative records of annual GHG emitted between 1990 and 2012. The graph indicates that there was a progressive increase in the quantity of GHG emitted from year to year between 1990 and 2007. However, there was a gradual reduction in the GHG emission between 2008 and 2012. The reduction in the value of the GHG emission in the USA between 2008 and 2012 was traceable to the global economic downtown between the affected years [166].

The Natural Resources and Infrastructure Division of UNECLAC in its 2010 bulletin publication entitled “Towards low carbon transportation infrastructures” reported that the transportation infrastructures contribute 13% of the overall greenhouse gases (GHG) emitted worldwide. The bulletin further states that the transportation sector also contributes 24% of the total carbon dioxide (CO_2) generated from the burning of fossil fuel. Records also show that the total emission from the

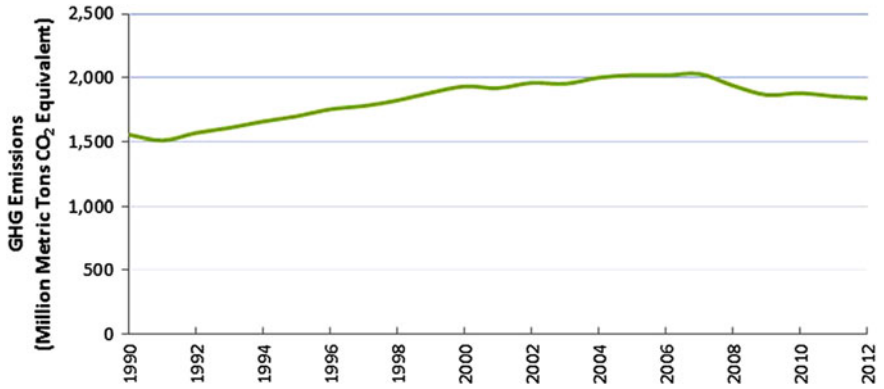

Fig. 5 A graph showing the greenhouse gases emission in the USA between 1990 and 2012. *Source* Sources of greenhouse gas emissions [166]

production of construction materials, construction, maintenance, and life cycle of road and railway contribute 76,922,792 and 42,449,402 kg CO_2, respectively [10].

Out of the total distance of 78,893 km of transportation infrastructures built in Asia over a period of 20 years, a total estimate of 792,000,000 tons of carbon dioxide was generated [10]. The 2005 World Bank record shows that the prospecting, exploration, material acquisition and haulage, and energy used by equipment and machinery all produced 4,427.05 tons of carbon dioxide equivalence per kilometer [47].

The carbon dioxide emission generated from installations of road furniture like guardrails, shoulders, curbs, median, and bridges contributes 46.4% of the total CO_2 emitted on the constructions of expressways and pavements for all the types of roads. This shows that the furniture repairs and rehabilitation have a critical influence on the emission of CO_2 on the environment [47]. The greatest factor contributing to the high yearly generation of GHG emission is the rehabilitation and repairs of roadway and expressway pavements. Over the years, the construction of the pavement profile follows the sequence: subsoil, gravel base, old pavement, tack coat, paving fabric, and finally the asphalt overlay. Recent advances in pavement construction have seen the engineer designing newly improved pavement structures which made considerations for green alternatives to the warm mix asphalt (WMA) in the form of standard hot mix asphalt (HMA) [147].

Thermal stresses have been identified as building up from the old way of pavement construction and the applications of load repetitions on the road. Recent researches have been considering the reinforcement of pavement materials such as soils and aggregates for the enhancements of improved, less hazardous pavement with health-monitoring tendencies [90].

Advances in pavement construction for about two decades have been on the suitability of geosynthetic materials for the reinforcement of soils and concrete. This is done with the expectation of enhancing reduction of the tensile stresses developed within the pavement structure [94]. Geosynthetics or geo-reinforcements are materi-

Fig. 6 Top left image shows geogrid reinforcement of a pavement layer, top right image shows woven geotextiles, and the bottom image shows the installation of geosynthetic materials for subgrade layer protection. *Source* Minnesota Department of Transportation [111]

als popularly used for transportation system constructions. They have the potentials to reduce propagation of cracks within the pavement structures. Originally, geosynthetic materials were made from polyesters and polyolefins. Recently, geosynthetic materials are now produced from fiberglass and rubber and are eco-friendly [59]. The vast quantities of geosynthetic materials consumed globally in the construction of pavements are manufactured by companies, such as: Tensar International Corp, Syntec, and Carthage Mills [62]. Figure 6 shows the geogrid or geotextiles types of geosynthetic materials as installed for pavement construction purpose [111, 147].

Geogrid shows great potentials for use as effective material for reinforcing base course layer of pavement consisting granular soils and aggregates [1, 2, 117]. Palmeira states that geosynthetics do not only reduce the tensile stress transfer within the pavement structure but also act as barriers to water and fines seepage. They also reduce rutting and differential settlements and rutting of the pavement to eventually extend the lifespan of pavement structures.

Equation 2 gives the efficiency metric for pavement reinforced with geosynthetic material as derived by the International Geosynthetics Society (IGS).

$$E = \frac{N_r}{N_u} \tag{2}$$

where E is the efficiency factor, N_r is the number of load repetitions up to failure for reinforced pavement, and N_u is the number of load repetitions up to failure for unreinforced pavement.

Civil engineering projects such as erosion control, foundation, external works and soil stabilization require adequate measures for the evaluation of the response or reaction of earth materials to dynamic and static loadings. This can only be done effectively on foundations, embankments, and pavement structures by conducting an important evaluation called the structural health-monitoring (SHM) system. The structural health-monitoring method could be deployed to effectively monitor pavement structures with the inclusion of sensor networks and statistical analyses for the SHM, including statistics and sensor networks [30, 49].

When the focus is strictly on the response pavement structures, the falling weight deflectometer (FWD) could be used to evaluate Young's modulus of elasticity for each layer of the pavement and comparisons after stipulated time (Long-Term Pavement Performance Program, [102]. The earlier mentioned geosynthetics are comparatively inexpensive to incorporate in pavement layers when compared with the FWD measurements; they geosynthetics can be used as sensors for data collection of the structural health-monitoring (SHM) system [183]. Successful determination of the stress and strain in pavement structures might require the use of conductive polymers. This also requires a perfect manufacturing process in order to maintain the accuracy of the mechanical competences of geosynthetics and geogrids which are available in commercial quantities so as to prevent the emission of greenhouse gases which are hazardous to the environment [166].

Polymers and plants have become recent most popular energy efficient, yet sustainable materials used worldwide for civil engineering purposes. Engineers have collaborated with chemists to evaluate fruits and vegetables for possible development of green polymers otherwise known as bioplastics [18, 42]. Green polymers are generally defined as biodegradable polymers derived from plants containing cellulose, starches, and sugars [18, 113]. Oil- and petroleum-based substances could be used as bonding agents to biodegradable green polymers. Polylactic acid, plant oil, polymer blends, and cellulose are the green polymers normally used as nanocomposites-based materials [113, 128].

Cellulose fiber stands out as a potential source for the extraction of biopolymers and could be prospected as an alternative to petroleum polymers. The quantity of cellulose polymer produced annually is 7.5×10^{10} metric tons. This makes cellulose polymer the most abundantly available natural polymer or biopolymer on the earth. Cellulose biopolymers are either derived from plants or organic substances; they are not only very economical but also possess lightweight. Since cellulose polymers are packed in nanocrystal forms, they have the very desirable tensile strength and stiffness parameters [32].

Moreover, cellulosic polymers are very economical and lightweight, yet they have very reliable stiffness and tensile strength parameters due to how their nanocrystals are packaged [32]. Cellulose possesses very high molecular weight and is infamous as a linear polymer made up of β-1,4 interconnected glucopyranose units, with polymer chains connected by hydrogen bonds making packs of fibrils (microfibrillar

aggregates), in vastly ordered expenses (i.e., crystalline phases), cellulose substitute with disordered domains [70, 79].

Carbon-based nanomaterials cannot be used directly, in their pure form, to treat water because they have a very small size which will be very difficult to recover from water treatment systems. Efforts are now being made to incorporate nanomaterials in synthetic polymer membranes or bound them unto surfaces of the membranes by covalent bonds between the functional groups present on the nanomaterials or by of physisorption on the membranes. Therefore, nanocomposite water treatment membranes have been successfully developed following the procedures earlier mentioned [151].

Shah et al. [144] investigated the changes in the nanostructure and nanoscale of local mechanical properties of cement pastes with both nano-modifiers and micro-modifiers. The micro-modifier used was silica fume while the nano-modified used was multiwall carbon nanotube (MWCNT). The results show enhancements of both mico- and nanomechanical properties of cement paste with the incorporation of carbon nanotubes (CNT). A similar trend was reported by Konsta-Gdoutos et al. [89].

The material properties of cementitious materials such as concrete are affected by the properties of the constituent materials at the nanoscale [114]. The fabrication of novel nano-sized fibers like CNTs has open a research for the reinforcement of concrete [39, 99, 104, 136]. Carbon nanotubes show enhanced mechanical properties when used with cementitious materials. However, the challenge with CNTs could be poor dispersion. This can be overcome by uniformly dispersing the CNTs within the matrix of the cement-based material [19, 68, 137, 180].

4 Established and Future Challenges

The setback to the purification of water with biopolymer is the challenge of synthesizing stable materials for the constant release of silver ions in the presence of complex contaminant deposits in drinking water which causes nanomaterial surfaces scaling [138]. Biopolymers like PE are biodegradable and as such can impact negatively on the environment. Agricultural products deployed for the production of bio-based feedstock, fuel used for tilling, harvesting, production, and conveyance of farm produces; herbicides and pesticides used for crop growth and protection; all have a negative impact on the environment. Petrochemical-based polymers have an impact on the environment too [184].

Geotechnical construction involves reclamation of the very large expanse of land. Deportation of microbial treatment could be a cost-effective method for land reclamation [76]. Identification of suitable or applicable microorganisms, screening, soil stability, biosafety of the application, optimization of microbial activity in situ, soil stability after biomodification, and cost-effectiveness are the main challenges faced at different locations where microorganisms are applied for geotechnical engineering [76, 112].

A future work could be done on the comparison of the effects of CNTs and silica fume on the mechanical properties of cement paste and bulk cement paste. Their effects on the C–S–H matrix and Young modulus could also be investigated. Though the natural fibers are basically considered as energy efficient and have the tendency to generate employment opportunities for citizens in the countries where they are produced, the challenges that may result are basically environmental such as competition with food crops, depletion of the nutrients in the soil as a result of protecting plants with herbicides and pesticides. The unpredictability of crop yields and properties with weather variations must also be assessed [186].

Hitherto, none of the biodegradable polymers has been used as a porous reinforcement material. However, if engineers could develop eco-friendly polymers, the design of flexible and improved earth materials in place of carbon-based materials would be achieved [156]. Acquisition and installation of SHM systems on civil engineering infrastructures are very expensive. It is easily adaptable more to bridge superstructures depending on its importance [67].

5 Conclusion and Future Trends

Like river sand, nanocomposites are characterized by very high shear strength in their loose and wet arrangements. The cost of nanocomposite water purifiers developed which produced safe and affordable drinking water for a family was USD 2.5 per annum. Adsorption-based means of purifying water is dependent on the generation or fabrication of materials composed in a nanostructured form close to ambient temperature [138]. Bacteria are used in aerobic tanks for the treatments of wastewater in water treatment plants.

Biopolymers do not harm farm produces neither do they have a huge impact on environmental disasters like transportation machinery and extraction of crude oil does. Moreover, the recycling of wastes from biomass and agricultural products contributes advantageously to environmental conservation, the balance of the ecosystem and environmental cleaning as against the destructive action of petroleum-based polymers [65, 66, 75].

New clay composite materials suitable for reinforcing constituents are emerging. The clay could be useful for construction purposes. High strength and ratio of stiffness to the weight of the composites could be used for low carbon vehicles which are environment-friendly that could prevail in the market with comparatively low cost. These newly developed nanocomposites could fulfill the desired properties and might not have ignitable characteristics [186]. Biopolymers and nanocomposites show great potential for civil engineering applications. They can be used for soil improvements, soil stabilization and irrigation and erosion control, improvement of the mechanical properties of cement- and concrete-based materials, building and for other construction. Different combinations of materials in as much as the CFF matrix, particulate and/or fiber can evaluate in various proportions to arrive at a hybrid composite. Mod-

ification of the existing material and improvement of its properties could lead to an improved highly and hybrid materials for fabrication and construction [14].

For the safety, sustainability of the environment and availability of natural materials are very important in modern developments and to engineering designs, fabrications, and constructions; there must be a focus on new generation materials (both raw and natural) for manufacturing and engineering developments. Without a doubt, further work is required on the size control and distribution of metal with other NPs in nanocellulose substrates. Small and dispersed metals could be evaluated for SERS applications with the aid of aggregated and large metal NPs. Nanocomposites can be evaluated for NPs loading. Investigations are also required for the utilization of inorganic materials in nanocellulose matrix as it might affect the sustainability of the nanocellulose.

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Chapter 16
Preparation, Characterization, Types and Applications of Polysaccharide Nanocomposites

S. Gowthami and S. Angayarkanny

1 Introduction

Polymers, which are produced by the living system, are called biopolymers. The biopolymers can be broadly classified into three categories: polynucleotide made with nucleotide monomers, polypeptides made with amino acid monomers and polysaccharides made with carbohydrate monomers. Apart from these broad categories, other biopolymers include rubber, the structural polymer like lignin and natural pigment like melanin.

Polysaccharides are having the advantage over other biopolymers such as polynucleotides and polypeptides in terms of its comparative thermal stability. Polysaccharides are having diversity in their structure with a lot of scope of various applications. Polysaccharides are available with extreme molecular weight variations, functionality variations ranging from monofunctional polysaccharides with only hydroxyl groups and multifunctional polysaccharides with the amine, carboxylic acid and hydroxyl groups. Polysaccharides also possess a elevated level of chirality, variation in water solubility ranging from soluble to insoluble variants, non-toxic properties and environmentally safe material made the biological advantages of polysaccharides to be used for the preparation of nanomaterials and nanocomposites.

Polysaccharides are going to be a biomass for the production of alternative fuel over fossil fuel [71]. The growing concerns over the depletion of fossil fuels made to think about alternative energy source because of their ready availability, economically viable and immense potential of polysaccharides. In addition to the prime importance of starch as a food material, it is also used for the nonfood applications and in medical applications such as polysaccharide-based hydrogels, proteoglycans, glycolipids and anticoagulant polysaccharides. Polysaccharides both physically and chemically modified variants have the advantage of being used in the conventional

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polymer processing equipment [56]. Because of the deprived mechanical strength, water sensitivity and thermochemical properties of polysaccharide, the application of them in the various fields is restricted. This problem can be overcome by using polysaccharide in the nanoscale reinforcing materials [10, 56, 77].

The advantage of preparing polysaccharide nanocomposite is that the filler of nanocomposite also can be from biomaterial which can be biocompatible as well as it will retain the biodegradability of the composite prepared. The nanocomposite we mean is the biopolymer incorporated with particles of nanoscale dimension in at least one direction, from bio-origin ending up in very high improvement in the mechanical strength even with less amount of incorporation [11]. Polysaccharide nanomaterials are produced from both the plant and animal origin from different sources like cellulose, starch, chitin, chitosan using different methods [16, 18]. For the preparation of polysaccharide nanocomposite, good interfacial interactions are anticipated as the nanoparticle filler and the biopolymer has a similar chemical structure, which is very important in the case of preparation of nanocomposite material. Since polysaccharides are having good water dispersibility, water dispersions of polysaccharide nanomaterials are generally obtained. The nanoparticle dispersion in water could be the best medium to form the nanocomposites; starch could form hydrogen bonds in water medium by breaking the intermolecular bonds and forming a gel structure with trapped water. This review intends to throw light in fields of preparation, characterization, types and applications of polysaccharide nanocomposites.

2 Polysaccharide Nanostructures

Cellulose

Cellulose is a straight chain macromolecule consisting of hundreds to thousands of b-D-glucopyranose units joined by glycosidic b-(1,4) bonds (Fig. 1). Cellulose monomer has six hydroxyl groups, so it is hydrophilic in nature and have water contact angle of 20–30°. The hydroxyl groups help them to form hydrogen bonding ability to have an intact structure which is the reason behind the crystallinity of the polymer. Cellulose forms microfibrils and nanocrystals by transverse cleavage during the acid attack of its amorphous regions [53]. Nanoparticles and nanofibrils from cellulose can be extracted by mechanical and chemical top-down approach in the deconstructing methodology. A high-pressure homogenization or grinding procedure is generally involved in the mechanical treatment [17]. Multiple mechanical shearing methods help the cellulose fibers to release individual nanofibrils of cellulose. Since cellulose is not soluble in both aqueous and non-aqueous solvents, aqueous dispersions of cellulose nanofibrils can be prepared. These nanofibrils are high-valued materials as it could give a very good fortification to the existing mechanical properties of the materials, and also it can act as an important unprocessed substance for the synthesis of unique materials. Cellulose nanofibrils form gel-like suspension in water. Generally, size of the cellulose nanofibers varies from 3 to 100 nm based on

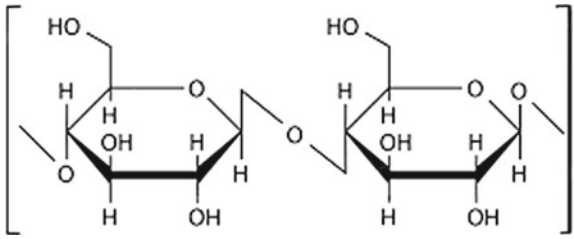

Fig. 1 Chemical structural representation of cellulose

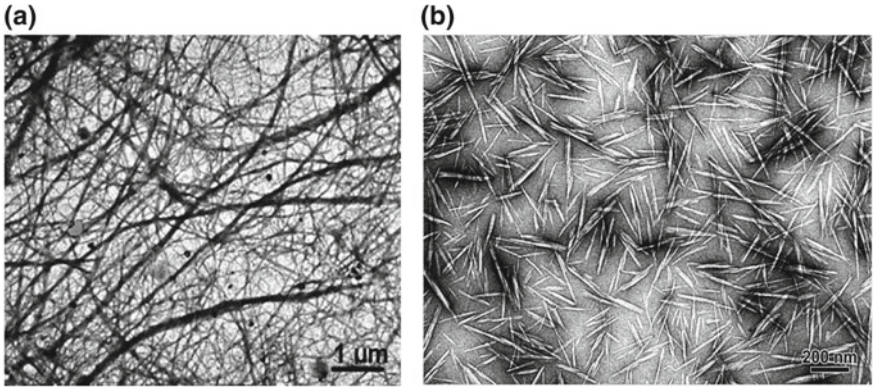

Fig. 2 Transmission electron micrographs from a dilute suspension of **a** cellulose nanofibrils from *Opuntiaficus-indica* [59], **b** cellulose nanocrystals from ramie fibers [26]

the source and method of production of the nanoparticle. The general defibrillation process yields cellulose fibers with more than 1 mm (Fig. 2a). The size is brought down by controlled hydrolysis of the fibers. The longitudinal cut of the cellulose microfibers is done by dissolution of amorphous domains of cellulose using strong acid hydrolysis treatment. The penetration of hydronium ions from acid hydrolysis into non-crystalline regions of the cellulose molecule facilitates the release of individual crystallite by glycosidic bond cleavage. The negatively charged groups formed by anionic sulfate ester group (formed by anionic sulfuric acid hydrolysis) enhance the dispersion of cellulose nanoparticle in water depending on the thermostability of the nanoparticles [54]. The dimensions of the nanofibers, that is, the aspect ratio of the nanofibrils, depend on the origin of substrate and reaction conditions. Figure 2b shows rod-like high aspect ratio nanocrystals.

Starch

Starch may be a chemical compound saccharide consisting of an outsized range of aldohexose units joined by glycosidic bonds. Two different polysaccharides are present in starch, a unit in starch is made of (1,4)-linked a-D-glucan amylose and (1,6)-a-D-glucan amylopectin (Fig. 3), each representing more or less 98–99% of the dry weight. This sugar is made by most of the plants as energy storage.

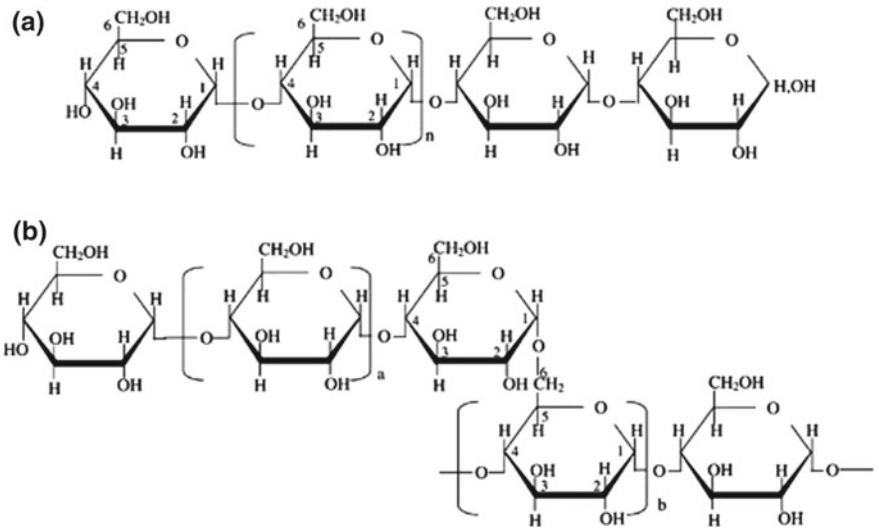

Fig. 3 Chemical structural representation of **a** amylose and **b** amylopectin

Increasing interest in the usage of starch for various purposes is because of its high abundance, economically viable, biocompatible, biodegradable and non-toxic nature [14]. Polysaccharides from varied categories possessing diverse properties are not applicable to identical applications [98]. Starch nanoparticles with different morphologies and sizes are prepared using various techniques involving regeneration and precipitation [44]. Nanocrystals of starch are produced by acid hydrolysis yielding crystalline starch nanoparticles which is a classical and most explored method of nanoparticle preparation [17]. The starch nanocrystals were prepared by 15 wt% of starch dispersion hydrolyzed by 3.16 M H_2SO_4 at 40 °C at constant stirring with 100 rpm for 5 days. It is shown that acid hydrolysis yields starch nanocrystals at very early stages from 24 h, and microsized and nanosized particles were found to coexist even in the final stages (Le Corre et al. 2011). Microfiltration unit equipped with ceramic membranes is used to separate the hydrolyzed starch suspension containing micro and nanosized particles (Le Corre et al. 2011).

Differential centrifugation was not found to be a suitable method to separate starch nanoparticles. The preparation methods were stabilized and reported with a statistical experimental design of multilinear regression analysis to propose a predictive model for the preparation of starch nanoparticle in one day (Le Corre et al. 2012). Starch on enzymatic pretreatment undergoes acid hydrolysis in short duration of time (Le Corre et al. 2012).

The transmission electron micrograph (TEM) (Fig. 4) of an aqueous suspension of waxy maize starch nanocrystals synthesized by hydrolysis using H_2SO_4. They exist as platelet-like particles having dimensions in the range of 5–7 nm by thickness, length ranging from 20 to 40 nm and width ranging from 15 to 30 nm [73].

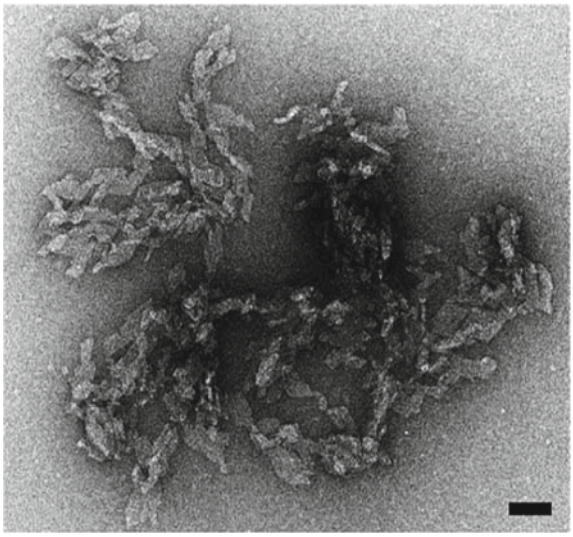

Fig. 4 Transmission electron micrograph (TEM) of starch nanocrystals (scale bar: 50 nm) [1]

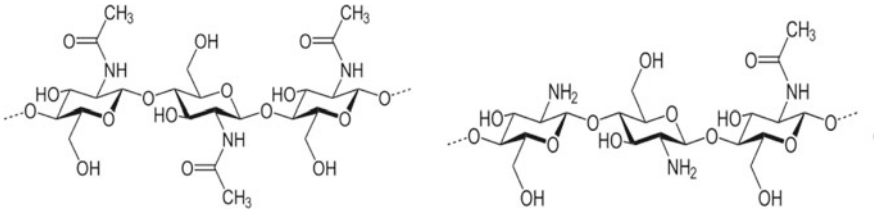

Fig. 5 Chemical structural representation of chitin and chitosan

Chitin and Chitosan

Chitin is the second ubiquitous natural macromolecule of carbon, which has a straight chain polysaccharide constructed by (1–4)-linked 2-acetamido-2-deoxy-b-D-glucopyranose units. It is a principal component of cell walls in fungi, the exoskeletons of arthropods, such as crustaceans. Though chitin does not show itself in organisms producing cellulose, these molecules are classified as cellulose derivatives [74] (Fig. 5).

Due to the hydrogen-bonded semicrystalline structure of chitin, it is readily hydrophobic in nature. Due to this reason, chitin is not soluble in most of the solvents. Chitin nanofibrils or chitin nanocrystals are prepared similar to the preparation of cellulose nanofibril or cellulose nanocrystals. These involve strong acid catalyzed hydrolysis or mechanical shearing respectively. Like cellulose nanocrystals, chitosan nanocrystals also occur as rod-like nanoparticles. TEM image (Fig. 6) of dilute sus-

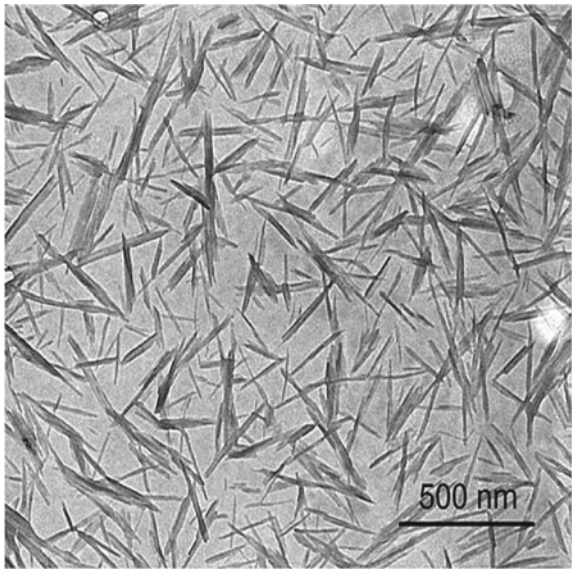

Fig. 6 Chitin nanocrystals from crab shell [25]

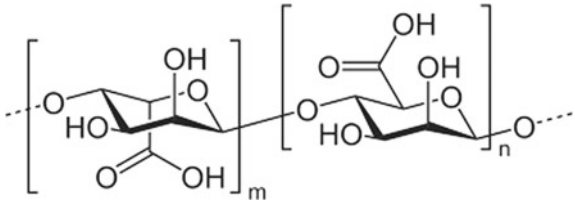

Fig. 7 Chemical structural representation of alginate

pension of chitin fragments from crab shell suspended in water [25] also shows rod like nanoparticles.

Chitosan is a linear sugar comprised of willy-nilly distributed deacetylated b-(1–4)-linked D-glucosamine and acetylated *N*-acetyl-D-glucosamine. Chitosan dissolves in aqueous acid at pH less than 6.5. Chitosan is prepared from chitin by partial deacetylation of chitin in extreme alkaline conditions. It is tricky to synthesize chitosan nanofibrils. Chitosan solubility in neutral and alkaline aqueous solutions can be amplified by introducing carboxymethyl groups at some amino and primary hydroxyl sites of the glucosamine units of chitosan construction, without disturbing other properties [14].

Alginate

Alginate is an anionic polysaccharide containing blocks of (1,4)-linked b-D-mannuronate (M) and a-L-guluronate (G)residues [49] (Fig. 7).

Due to the presence of calcium ions, alginate hydrogels formed by ionic crosslinking are widely used in biomedical applications because of their biocompatible prop-

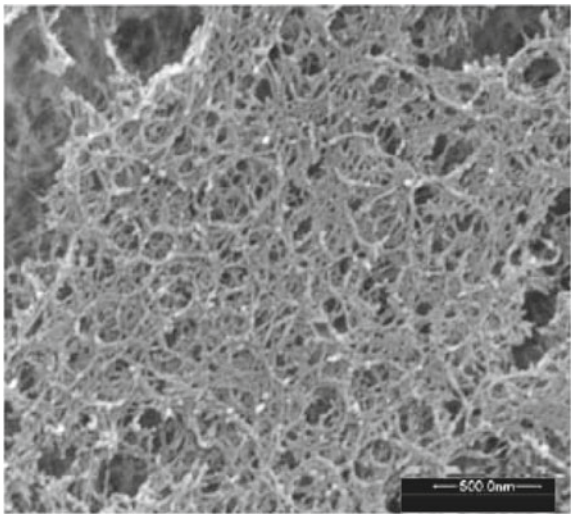

Fig. 8 FE SEM image of alginate hydrogel [75]

erties. Alginate requires comparatively simpler and gentler fabrication conditions to preserve the biological activity of proteins and cells encapsulated in alginate [38] (Fig. 8).

The chemical properties of the polymers can be improved by making changes in the structure of polymers for required applications. Since C-2 position in alginate is suitable for modification in a simpler way, specific modification was done for chemical organization of alginate. The nanosized alginate is prepared from its aqueous dispersions [87]. Alginate nanocrystals were prepared from pluronic-based nanocarrier template.

3 Preparation of Nanocomposites

In order to show the special functions of nanoparticles in a compound matrix, incorporation of them in a matrix as composite structures is the most common strategy employed widely. This not just solely stabilizes the nanoparticles but also conjointly highlights the useful combinational assembly of nanoparticles and polymers. However, the preparation of nanocomposite structure majorly depends on the compatibility between the nanoparticles and polymer constituents that are involved in the construction. Thus, various techniques are being employed in the fabrication of nanocomposites to optimize a variety of parameters and attain a product with preferred properties that is perfect for the intended end function. Polysaccharide nanocomposites are prepared by a number of ways like film casting, physical mix-

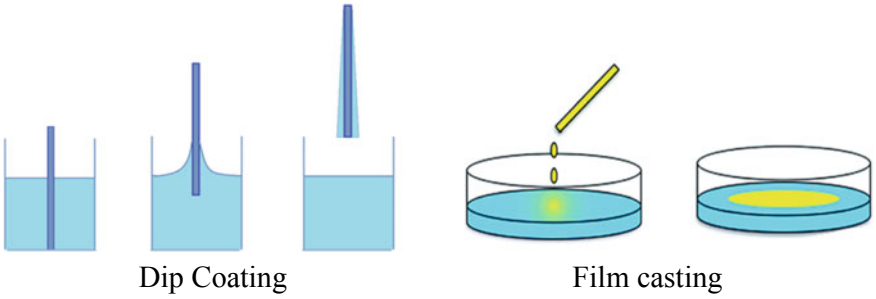

Fig. 9 Schematic illustration of film casting and dip coating

ing, dip coating, extrusion, hot pressing, foaming, extrusion blending, melt mixing, layer-by-layer assembly, gelation, co-precipitation and covalent coupling.

3.1 Physical Methods

Polysaccharide-based nanocomposites are fabricated by means of common physical methods such as film casting and dip coating. This is used in preparation of flexible nanocomposite films. Literature on film casting and dip coating method-based nanocomposite fabrication methods are discussed (Fig. 9).

Film casting of *N*-methyl morpholine-*N*-oxide yields uniform dispersion of cellulose with carbon nanotubes [39]. The nanocomposite of cellulosic paper is prepared by single-walled, multi-walled carbon nanotubes (MWCNTs) grown on silicon substrates using chemical vapor deposition which is used for the preparation of flexible energy storage devices. MWCNT is formed by the infiltration of cellulose solubilized in ionic liquids at room temperature [72]. Enhancement of thermal and mechanical properties is observed in nanocomposites fabricated by the integration of nanofibrillar cellulose in pullulan cast films. Addition of glycerol shows further improvement in malleability and additional mechanical properties [86]. Chitosan and bacterial cellulose are prepared by casting film from aqueous acetic acid [21]. Outstanding thermally conductive, transparent nanocomposites can be made by reinforcing cellulose nanofibers in epoxy resin through simple film casting processes [79].

3.2 Layer-by-Layer Assembly

Layer-by-layer assembly is a distinctive construction strategy used for the preparation of nanocomposites. Two different nanomaterials are alternatively stacked as layers over each other to obtain a nanocomposite structure that possesses the benefits from both the nano-constituents involved in the assembly. Few literature reports on the

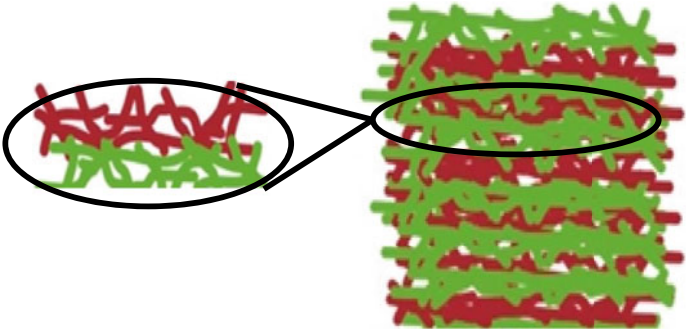

Fig. 10 Schematic illustration of layer-by-layer assembly

preparation of nanocomposites using layer-by-layer assembly strategy are discussed in this section (Fig. 10).

Addition of stratified salt in electrostatically structured polyose film of alginate reinforced with chitosan-coated polyose nanofibrous electrospun mat inhibited the growth of microorganisms in a layer-by-layer assembly [12]. Mediator-less biosensors are developed by layer-by-layer assembly of coatings of mucopolysaccharide with carbon nanotubes (CNTs), followed by a nursing accelerator layer and a final Nafion layer [22]. Polyanion/polycation complexes are also facilitated using layer-by-layer assembling methodology. Here, electrospun fibrils of chitosan/poly(ethylene oxide) blends are prepared by immersing the fibrils in hyaluronic acid solution [58]. Cellulose–chitosan hybrid nanofibrils was prepared by electrospinning their ester derivatives followed by hydrolysis under alkaline conditions [13].

3.3 Colloidal Assembly

The electrostatic aggregation of the polymers leads to the formation of a colloidal assembly. A report on colloidal assembly of polymers and nanofibrils in the formation of nanocomposites is discussed. A colloidal assembly (Fig. 9) of ionically stabilized biomimetic nanocomposites is formed by the micellization of anionic cellulose and cationic synthetic polymer [93] (Fig. 11).

3.4 Hydrogelation

Fabrication of nanocomposites by the hydrogelation of one of the nanomaterials with the simultaneous incorporation of the other is known as hydrogelation. Supramolecular hydrogelated nanocomposites constructed of cyclodextrin macromolecule and

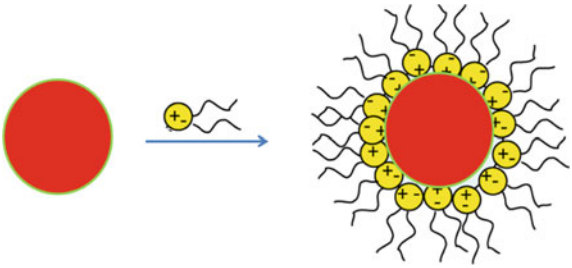

Fig. 11 Schematic illustration of colloidal assembly

polysaccharide nanocrystals showed quick gelation times, with improved mechanical properties, and were intended for sustained drug release in drug delivery applications [97]. Diffusion of solvent of heparin and pluronic yields spontaneous emulsions that afford heparin-functionalized nanoparticles for releasing the controlled growth factors [9]. Monoclonal antibodies delivery was explored with trimethyl chitosan nanoparticles [92], and gel formed from chitosan-hyaluronic acid nanoparticles loaded with heparin is studied for the treatment of asthma [67].

3.5 Co-precipitation

Co-precipitation is a simultaneous precipitation technique wherein the constituent components of a nanocomposite precipitate out to form the final structure. Co-precipitation technique is used in the synthesis of drug loaded, pectin-coated, iron oxide magnetic nanocomposite for removal of copper ion [24]. Co-precipitation of iron oxide coated with nanoparticles is used for the targeted delivery of anticancer drugs [32].

3.6 In Situ *Nanoparticles Preparation*

In situ nanoparticle formation in nanocomposite structures ensures consistent distribution of nanoparticles in matrix as well as excellent compatibility between nanoparticles and polymers. The existence of a polymer network during the formation of nanoparticles affords a higher stability of the nanoparticles being formed thereby aiding them in staging their functions more efficiently. Hydroxyapatite/bacterial polysaccharide nanocomposite scaffolds are prepared by biomimetic techniques for apatite formation [20] (Fig. 12).

Silver nanoparticles incorporated cellulose nanocomposites with excellent antibacterial properties are fabricated by solution mixing of cellulose and Ag salts followed by chemical reduction or UV-based reduction [70]. The cellulose fibers are decorated with $CaCO_3$ nanoparticles using in situ formation of $CaCO_3$ nanopar-

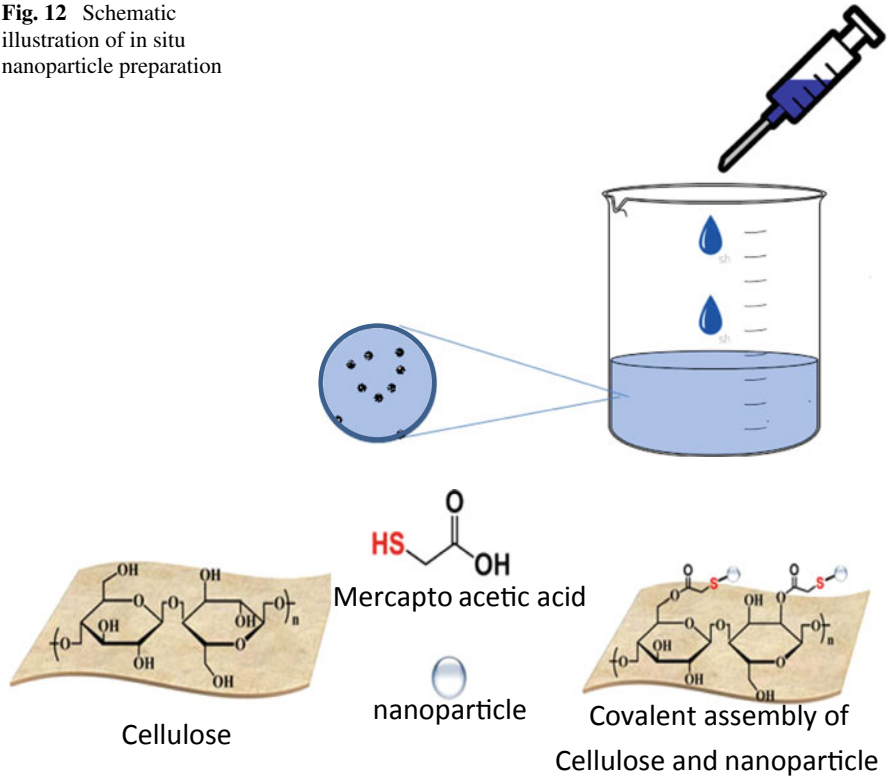

Fig. 12 Schematic illustration of in situ nanoparticle preparation

Fig. 13 Schematic illustration of covalent assembly of nanoparticle with cellulose

ticles by adding NaOH solution to $CaCl_2$ and dimethyl carbonate in the presence of cellulose fibers [90]. CO_2 and $CaCO_3$ form along with nanoparticles on cellulose during the addition. In situ formed ZnO nanoparticles reinforced alginate-based nanocomposites are widely exploited for their antibacterial applications [84].

3.7 Covalent Coupling

Covalent pairing of nanoparticle with polymer leads to nanocomposite formation. The bioactive ligands or modifiers covalently linked to nanomaterials are used to fabricate polysaccharide-based nanocomposites (Fig. 13).

There are several literature reports on covalent assembly of nanocomposites. Cellulose modified with thiol fabric with silver nanoparticles for good antimicrobial activity or chitosan redox grafted to Ag nanoparticles are few examples of this kind. To cite a few of the reports [69].

3.8 Co-synthesis

Simultaneous synthesis of the constituents in a nanocomposite right during the construction of the composite structure produces a product with exceptional compatibility between the constituent moieties. The dry films exhibit antibacterial traits are expressed in the sheets due to the coordination of Ag nanoparticles to chitosan amino groups which is enabled by thermal reduction of the sheets [94]. Stabilized Au and Ag nanoparticles are synthesized by the reductive amination using 2,6-diamino pyridinyl heparin (or hyaluronan) [48]. Au nanoparticles are synthesized in situ using guar gum wherein the polymer matrix acts as both a reducing and a capping agent [68]. Nanocomposites containing silver can be prepared by microwave synthesis by microcrystalline cellulose as reducing, stabilizing and supporting agent [80]. Galactomannan polysaccharides can be used in controlled Au nanoparticles formation [50].

4 Characterization of Nanocomposites

The morphological and structural investigation of nanocomposites was done using the techniques like visual inspection, scanning electron microscopy, X-ray diffraction, FT IR, thermal properties, water permeability and biodegradability studies.

4.1 Visual Inspection

The mechanical property of the composite increases by the addition of nanofillers, but the transparency of the nanocomposites reduces because of the scattering of light by the randomly dispersed nanofillers. The transparency of the film can be maintained more effectively by making the nanofillers to be present in the matrix of the composite.

4.2 Scanning Electron Microscopy

Surface morphology of the prepared nanocomposite is monitored by scanning electron microscopy. The comparative surface morphological dimensions of the unfilled matrix and the nanoparticle reinforced composite structure and the effect of reinforcement in the reduction of fracture at the surface level in the polymer matrix can be understood by cryo-fractured surfaces. The brittle structures by cryo-fractures also evidence on plasticization of the composite by nanoparticles, homogeneity of the

nanocomposite, nanoparticle dispersion in the matrix, voids and aggregates present in the matrix and alignment of the nanofillers in the matrix.

4.3 X-ray Diffraction Analysis

X-ray diffractometry of nanocomposite structure reveals the crystallinity or the amorphous nature that the product possesses. The XRD of thermoplastic starch (TPS) prepared in the dry condition shows a broad peak centered around 18–20° revealing its fully amorphous nature [2, 3, 61]. The water content of the starch is observed in X-ray diffractometry through an amorphous broad hump, which shades off progressively with increase in water content of the material [3].

4.4 Fourier Transform Infrared Spectroscopy

The functional groups of material can be identified using FTIR. Nanocomposites show similar FTIR spectrum because of the functional group similarity of the polysaccharide nanofiller and the matrix. However, the stretching vibration of hydroxyl (–OH) group shows shift or broadening as a result of formation of new hydrogen bonding based on interactions between the polysaccharide molecules of nanocomposites [5, 6, 19, 23].

4.5 Thermal Properties

Thermal properties like glass transition temperature, melting point and thermal stability of the polymeric materials are very significant for determining the processing conditions and its applications. The thermal properties are determined using DSC while the thermal stability is assessed using TGA.

Transition Temperature

Glass transition temperature (T_g) can be classically determined by DSC. T_g can also be measured from dynamic mechanical analysis (DMA) from its relaxation process. Thermoplastic starch plasticized with glycerol showed low T_g for glycerol-rich domains and high T_g for starch-rich domains [3].

Melting and Crystallization

The melting point, crystallization temperature and degree of crystallinity of polymeric materials can be determined using DSC. Molecular mobility of macromolecules can be monitored using DSC, and plasticization effect of starch in moist atmosphere and crystallization of amylopectin chains are monitored using DSC

[3]. The presence of cellulose nanocrystal [61], cellulose nanofiber [33] or starch nanocrystal [89] is found to increase crystallinity of starch. The crystallinity increases because of nucleating agent effect of the nanofiller toward the starchy matrix. With increase in the size of crystals formed, the melting point shifts toward higher temperatures [41, 89].

Thermal Stability

Thermal stability of the materials is monitored by recording the weight loss as a function of temperature by heating rate in inert atmosphere in TGA. Water content of hydrophilic polysaccharide materials such as starch can be determined by loss of moisture from 100 °C. The nature of moisture present in the material whether it is easily evaporating moisture, compositional water or water intimately bound to the material constituents can be identified using TGA.

4.6 Mechanical Properties

The important aspect of using nanoparticles in polymeric matrices is the improvement of the mechanical properties. Linear mechanical behavior of materials is analyzed using dynamic mechanical analysis (DMA) with very broad temperature/frequency variation. Linear mechanical behaviors are very sensitive to the morphology of the heterogeneous systems.

4.7 Swelling and Barrier Properties

High hygroscopicity of polysaccharides, especially starch, makes them to exhibit poor water barrier properties. Source, preparation conditions and storage of the polysaccharide films can control the swelling and barrier properties. Plasticizers are added to the polysaccharide films to reduce its brittleness; unfortunately, plasticizers decrease the global barrier properties. This problem with plasticizers can be overcome by the addition of nanoparticles. Nanoparticles improve the barrier properties due to their small size, significantly greater surface-to-volume ratio. Highly crystalline nature of most of the polysaccharide nanoparticles and their ability to form a dense network increases the low permeability of the nanocomposites.

4.8 Water Solubility

The water solubility requirement of polysaccharide composite film highly depends on the applications. Water solubility is must for application like food additive or

encapsulation of food or medicine, whereas water resistance is required for packaging applications to enhance the product integrity.

4.9 Water Absorption

The water uptake of polysaccharide-based material is determined gravimetrically as a function of conditioning time: M_t

$$\text{Water uptake}(\%) = \frac{M_t - M_o}{M_o} \times 100$$

where M_t and M_o are the weights of polysaccharide-based material after molding for a time t and initial dry weight, respectively. The absorption rate is fast at initial time, and it stabilizes for longer times, giving the water uptake at equilibrium corresponding to a water uptake value M_1. At short times $[M_t - M_o]/M_\infty \leq 0.5$, the water diffusivity or diffusion coefficient D through a film of thickness $2L$ can be estimated using the following equation:

$$\frac{M_t - M_o}{M_\infty} = \frac{2}{L}\left(\frac{D}{\pi}\right)^{1/2} t^{1/2}$$

by plotting $(M_t - M_o)/M_\infty$ as a function of $\left(\frac{t}{L^2}\right)^{1/2}$.

4.10 Biological Properties

Biodegradability

Biodegradation of the polymer is decided by the nature of organism for degradation and type of pretreatment of the polymer in addition to polymer characteristics. Both natural and synthetic plastics can be degraded by microorganisms such as bacteria and fungi [4]. Biodegradation of polysaccharide-based samples is monitored by the liberation of CO_2 from the mixture of the polymer with compost soil. The rate of biodegradation can be monitored from the amount of CO_2 released. The decomposition of the polymer matrix can be delayed with incorporation of polymer nanoparticles.

Antifungal/Antimicrobial Properties

The antifungal and antimicrobial properties are required for the polymer nanocomposites when it is used for the packaging applications. The starch nanocomposite with chitosan nanocrystal and chitosan nanofibril was reported to have antifungal

activity against as per gillusniger [76]. Chitosan nanofibril was found to have better inhibition effect compared to chitosan nanocrystal.

5 Types of Polysaccharide Nanocomposites and Their Applications

The polysaccharide nanocomposites are classified based on the composition of the polysaccharide with other materials. There are several applications are reported for the polysaccharide nanocomposites. The applications of polysaccharide-based nanocomposites are reported huge in recent years. To site few, a list of components and their applications are presented in Table 1.

6 Polysaccharide Nanocomposites—Biomolecule

Polysaccharide nanocomposites in combination with biomolecules exhibit number of applications in the biomedical fields. A biomimetic living matrix for cell growth is prepared using electrospun collagen–chitosan nanofibrils crosslinked using glutaraldehyde vapors [7]. Biocompatible tissue engineered scaffolds were prepared from electrospun collagen–chitosan–thermoplastic poly(urethane) blends. Nanofibrils of collagen or chitosan formed by electrospinning could provide a good support for the growth of both endothelial cells and smooth muscle cells, thereby used as a scaffold in tissue engineering [27]. This nanocomposite depicted sustained release of bone morphogenetic protein-2 (BMP-2) for bone tissue engineering. Fibrous membrane with protein characteristics can be obtained from the blend of hyaluronan and gelatin formed by electrospinning [51].

Polysaccharide nanocomposite drug delivery system is designed by hydrophobic modification of the polysaccharides using crosslinking, both covalent and ionic and with addition of polyelectrolytes [55].

7 Conclusions and Future Scope

Polysaccharides are most abundant organic materials in nature. Polysaccharide nanocomposites reinforced with other materials and polysaccharides itself will be a potential material for future research. The inherent biodegradable property and abundance of polysaccharides make them as material of choice for eco-friendly packaging films or sheets. The mechanical property of polysaccharide can be altered by making nanocomposites using suitable additive material and suitable method of preparation

Table 1 Polysaccharide nanocomposites, constituent polysaccharide with additive and their specific applications

Polysaccharide	Additive	Applications	References
Starch	ZnO	Antibacterial and UV protection cotton fabrics	Vigneshwaran et al. [88]
	Polyaniline	Removal of reactive dyes from synthetic effluent	Janaki et al. [31]
	Cellulose	Packaging materials and biomedical materials	Svagan et al. [81]
Chitosan	Ag	Antibacterial	Travan et al. [85]
	[Fe(pz){M(CN)$_4$}] (M = Ni, Pd, Pt)	Spin-crossover properties	Tokarev et al. [83]
	Poly(lactide-co-glycolide)	Tumor imaging and therapy	Chung et al. [8]
	Collagen	Tissue engineering	Huang et al. [27], Chen et al. [7]
	Heparin	Tissue engineering	Volpato et al. [91]
	Bacterial cellulose	Casting food packaging and electronic displays	Fernandes et al. [21]
	Alginate	Tissue engineering	Schmidtke et al. [78]
Cellulose	Ag	Antibacterial	Pinto et al. [70]
	CNTs	Energy storage devices	Pushparaj et al. [72], Miyauchi et al. [65]
	Graphene	Electronic devices	Luong et al. [57]
	$CaCO_3$	Fillers in industrial polyethylene matrixes	Vilela et al. [90]
	CdS	Energy production: photo catalytic H_2 production	Ke et al. [34]
	TiO_2	Industrial papermaking	Marques et al. [60]
	ZnO	Multisource energy conversion	Kumar et al. [40]
	Lysostaphin	Wound healing	Miao et al. [62]
	Poly(*N*-vinylcaprolactam)	Protein affinity purification	Webster et al. [95]
	Organic rectorite, chitosan, sodium Alginate	Antibacterial	Deng et al. [12]

(continued)

Table 1 (continued)

Polysaccharide	Additive	Applications	References
	Quaternized poly(1,2-butadiene)-block poly (dimethylaminoethyl methacrylate)	Biomimetic nanocomposites	Wang et al. [93]
	Hydroxyapatite	Bone tissue engineering	Fang et al. [20]
	Polyvinyl alcohol	Tissue engineering	Millon et al. [64]
Hyaluronan	Ag	Antibacterial	Kemp et al. (2009)
	CNT	Biosensing	Filip et al. [22]
	Gelatin	Tissue engineering	Li et al. [51]
Heparin	Ag	Antibacterial	Kemp et al. (2009)
	Au	Antibacterial	Kemp et al. (2009)
	CNTs Coupling of activated heparin to nanotubes	Blood compatibility nano devices	Murugesan et al. [66]
	Fe_3O_4	Targeted drug delivery	Javid et al. [32]
	Poly(glycolide-co-lactide)and pluronic	Drug delivery	Chung et al. [9]
	Poly(L-lactide-co-e-caprolactone)	Vascular tissue engineering	Kwon and Matsuda [42]
	Poly(lactide-co-glycolide), pluronic Gelatin	Tumor imaging and therapy	Chung et al. [8]
	Gelatin	Bone tissue regeneration	Duan and Wang [15]
Chitosan/heparin	Activated carbon beads	Removal of chemotherapeutic, doxorubicin	Miao et al. [63]
	Fe_3O_4	Low-density lipoprotein removal	Li et al. [52]
	Fe_3O_4, Au, Tween 80	Magnetic resonance imaging with a tumor-targeting	Yuk et al. [96]
	Bovine jugular veins	Tissue engineering	Tan et al. [82]

(continued)

Table 1 (continued)

Polysaccharide	Additive	Applications	References
Chitosan/hyaluronan	Heparin	Drug delivery	Oyarzun-Ampuero et al. [67]
Hyaluronan/heparin	Steel	Drug eluting stents	Huang and Yang [30]
	Cellulose and chitin whiskers, platelet-like starch cyclodextrin	Drug release	Zhang et al. [97]

as discussed in this chapter with many reported references. The mechanical property of nanocomposites can be varied from damp proof foam to structural material.

The biomaterials can also be explored to find application in the fields of food science and their related health and safety impacts on the environment. The optimization of the material synthesis is to be done extensively to get solutions for the issues like biocomposites with tunable properties by material engineering methodologies. Polysaccharides are abundant in nature and offer significant properties in synthesis, fabrication and structure. Applications range from biomaterials to electronics and other industrial uses. Polysaccharides-based nanocomposites are also a "green" alternative to oil-based synthetic polymers.

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Chapter 17
A Review on Versatile Applications of Degradable Polymers

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1 Introduction

The synthesis of Bakelite in 1907 marked the beginning of polymer age [1]. Since then, thousands of synthetic polymers have been synthesized and used in numerous applications. Polyethylene terephthalate (PET) is the largest produced synthetic non-biodegradable polymer. Apart from synthetic polymers, thousands of natural polymers exist. Cellulose is the largest natural polymer available which is derived from a plant source. Deoxyribonucleic acid (DNA), the natural protein, is another example of a natural polymer. Celluloid is the man-made polymer of cellulose origin.

To date, 8300 million metric tons (Mt) of virgin polymers have been produced. Out of which about 9% recycled and the remaining accumulated in the natural environment [2]. By 2050, estimated synthetic polymer production is 12,000 Mt. Imagine the quantum of plastic waste that would accumulate in a natural environment without degradation if left unattended. Considering the impact of these non-biodegradable wastes on nature, the best possible proactive approach is developing fast degrading polymers and maximum utilization of natural polymers.

The concept of biodegradable polymers started in the 1980s and as on 2017 annual production of degradable plastics is 2.05 million tons. 58% of the biopolymers are consumed by the packaging industry and 11% by textiles [3]. In this chapter, a brief introduction to degradable polymers followed by an extensive review of versatile applications of these polymers is presented.

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2 Degradable Polymers

2.1 Definition

European standard DIN EN 13432, the US standard ASTM D 6400 and the Japanese GreenPla standard defines requirements for biodegradable and compostable polymers. Apart from biodegradability, a polymer can degrade by several methods other than bacteria, enzymes, or any different biomechanics. In a broader sense, to manage a used polymer until end-of-the life, any approach can be adopted without adversely affecting the environment. IUPAC in its gold book defines the broader view of polymer disintegration. According to IUPAC biodegradation/degradation defined as follows,

1. Polymer susceptible to degradation by biological activity, with the degradation accompanied by a lowering of its molar mass (Biodegradation) [4, 5].
2. Chemical changes in a polymeric material those results in undesirable changes in the values of in-use properties of the material (Degradation).
    a. In some cases, degradation is accompanied by a lowering of molecular weight.
    b. Causes of degradation may be specified by prefixes or by adjectives preceding the term degradation.

For example, degradation caused by exposure to visible or ultraviolet light is termed photodegradation; degradation induced by the action of oxygen or by the combined action of light and oxygen is termed oxidative degradation or photooxidative degradation, respectively; degradation induced by the action of heat or by the combined effect of chemical agents and heat is termed thermal degradation or thermochemical degradation, respectively; degradation induced by the combined action of heat and oxygen is termed thermo-oxidative degradation (Reproduced from IUPAC standard) [4, 6].

In either biodegradation or thermo- or photodegradation, the end result should not have any adverse effects on the environment for sustainable growth. Throughout the chapter, the broader approach of IUPAC is followed to highlight the novel and versatile applications of degradable polymers.

2.2 Classification of Degradable Polymers

On the basis of origin, degradable polymers are classified as synthetic and natural. Figure 1 shows pictorial overview of the classification of degradable polymers. Most of the available polymers come under these two classes. The route of synthesis, the presence of additives which aides in degradation, solubility in water and polymer blends, classifies the degradable polymers further [7]. Table 1 presents an overview of the classification of synthetic degradable polymers.

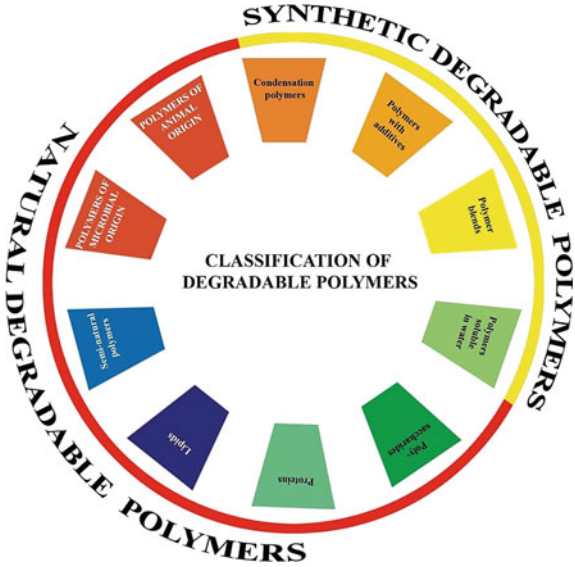

Fig. 1 Classification of degradable polymers

Table 1 Classification of degradable synthetic polymers

Synthetic polymers		
Polymer classification	Example	Degradation mechanism
Condensation polymers	Polyesters, polyurethanes, polyamides, polyanhydrides, polyureas	Hydrolysis under aqueous conditions, microbial or enzymatic action
Polymers with additives	Pro-oxidant or photosensitizer added to polymers. (e.g.) addition of Mn^{2+}/Mn^{3+} to polyolefins	Oxidation due to heat or light
Polymer blends	Blended with natural or water-soluble polymers	Both chemical and microbial action
Polymers soluble in water	Poly(ethylene glycol), Poly(vinyl alcohol)	Primarily by microbial action

Table 2 presents an overview of the classification of synthetic natural polymers. The polymers under this class are derived from nature and possess excellent biodegradability. Hence, it is considered safe for most of the applications. This class of polymers is recycled by natural mechanisms.

All these degradable polymers are widely used in biomedical applications, agriculture, packaging, pharmaceuticals, personal care, and housewares [8, 9]. The current chapter presents the versatile applications of all these types of polymers.

Table 2 Classification of degradable natural polymers

Natural polymers		
Polymer classification	Examples	Degradation mechanism
Polysaccharides	Cellulose, Starch, chitin, alginate, hyaluronic acid	Degradation by hydrolysis, enzymatic action, or microbial action
Proteins	Industrial protein from corn (zein), casein, wheat gluten, soy protein	
Lipids	Triglycerides	
Seminatural polymers	Polylactic acid, polyhydroxyalkanoates (PHA), chitosan	
Blends of natural polymers	Blends of PLA, PHA with starch, cellulose, chitin	

Fig. 2 Various applications of degradable polymers

3 Applications of Degradable Polymers

3.1 Degradable Polymers in Agriculture

See Fig. 2.

Improving agriculture productions is one of the essential requirements to sustain a quality life. Several technologies are attempted to increase agricultural yield by the development of effective pesticides, low water consumption, and crops grown under various climatic conditions. In 1950s, the use of plastic films (mulch) to reduce plant growth time and improve yield was attempted. Since then mulching become a successful technology which provides multiple benefits such as insects and weed control, reduce water evaporation, minimize soil erosion, increase in or maintaining soil temperature, and prevent soil splashing on vegetables and fruits. Apart from mulching,

plastic films are used for greenhouses and silage. The uses of polymers/plastics in agriculture become known as plasticulture [10].

With the global use of agricultural plastics, the success of plasticulture increased. In 2019, the demand expected to grow by 69% (7.4 million tons per year) [11]. Given the world's population and need for food, plasticulture is unavoidable in agriculture. The volume of polymer waste generated in farming is enormous. Due to soil contamination of the films, the recycling is restricted. Often the used films are land filed. The plastic fragment released into the soil accumulates over time and removing these films is a difficult task. Over a period, these plastic fragments from all the sources end up in the sea.

Ideal mulch must not have an adverse effect on the environment, provide a conducive climate for plant growth, intact throughout the crop cycle, and undergo complete degradation after composting either by microorganisms or photodegradation.

Low-density polyethylene (LDPE) currently used in agriculture mulching applications is not degraded instantly in the environment [12]. To overcome the non-environment-friendly properties of LDPE, new materials with biodegradability as required by standards ISO 17088 and ASTM D6400 emerged. As per these standards, 90% of these materials should be degraded to CO_2 within the specified time to be accepted as degradable materials.

3.2 Degradable Mulch in Agriculture Applications

Natural mulches are unpopular in agriculture because of its limited availability, inconsistent quality and labor it consumes for spreading [13]. Pine straw mulch, hardwood mulch, and hay mulch are examples of natural mulch. Polyethylene mulches are by far widely used synthetic material in agriculture uses. Easy processability, durability, less toxic nature, and excellent chemical resistance are the good features of polyethylene [14]. Low-density polyethylene, linear low-density polyethylene, and high-density polyethylene are commonly used in agricultural applications. Though very successful in agricultural applications, the non-biodegradability makes this polymer as a major environment pollutant [15]. Paper mulches, foam mulches, and hydramulch are alternated attempted to replace polyethylene [16, 17]. These mulches are less stable, and large volume production is difficult. A practically viable solution is the development of photodegradable and biodegradable materials to replace petroleum-based plastics.

Photodegradable plastics degrade by photo-initiated chemical reactions. A major issue associated with this kind of materials is incomplete conversion to CO_2 and water [18]. Later, polyethylene–starch composite-based sheets made as an alternate to degrade under light [19]. Polyurethane, polyester, polyethylene with cornstarch are some of the biodegradable polymers used for agricultural applications [20].

Polyesters are successful biodegradable polymers developed for agricultural use. Classification of polyesters is summarized in Table 3.

Table 3 Classification of polyesters

Polyesters		
Natural polyesters	Synthetic polyesters (non-renewable)	Synthetic polyesters (renewable)
Polyhydroxyalkanoates (PHA)	Polybutylene succinate (PBS)	Polylactic acid (PLA)
Polyhydroxybutyrate (PHB)	Polycaprolactone (PCL)	
Polyhydroxyvalerate (PHV)	Polybutylene succinate adipate (PBSA)	
Polyhydroxyhexanoate (PHH)	Modified PET	
	Aliphatic–aromatic copolyesters (AAC)	
	Polybutylene adipate/terephthalate (PBAT)	
	Polymethylene adipate/terephthalate (PTMAT)	

Environment compatibility, melt processability, good mechanical properties, and biodegradability make PBS one of the commercially successful polymers in agricultural use [21]. The biodegradability of PBS in soil [22] and compost [23] demonstrated the excellent usability of this polymer in plasticulture. Mulch films based on polybutylene adipate-co-terephthalate in various colors also successfully used [24, 25]. Polar nature and water solubility of polyvinyl alcohol makes this polymer easily blendable with starch and find use as mulch films [26].

3.3 Polymers in Other Agricultural Uses

Polymers in Agrochemicals Delivery

Better yield in agriculture is possible with the use of superior agrochemicals. However, use of the agrochemicals by conventional methods lack selectivity and uncontrolled release to the environment which leads to the exposure of these chemicals to the environment in large quantities. Environment-friendly, biodegradable polymer-based controlled release agricultural formulations would solve the issues faced in conventional techniques. Natural polysaccharide-based agroformulation is successful in this area [27]. The agroformulations employed in agriculture in the form of hydrogels, micro/nanobeads, and nanoparticles. The main advantage is minimal impact on the environment and degradation. Normally, in controlled release formulations, the active ingredient is incorporated into a carrier, normally a polymer. In conventional practice, the active ingredient is released to the environment immediately [28]. Due to biocompatibility, biodegradability and hydrophilic nature, bio-based polymers are gaining considerable acceptance as agrochemical delivery systems [29].

Alginates [30], starch [31], cellulose [32], cyclodextrin [33], and chitosan [34] are some of the polysaccharides used in agrochemical controlled release applications. In another advancement, pesticides encapsulated in nanoparticles exhibited a modified release profile than microparticle-based formulation [35]. In fertilizer release, chitosan-coated NPK fertilizer showed promising results [36].

Biocide Polymers

Biocidal polymers are macromolecules capable of killing or inhibiting the growth of microorganisms such as bacteria and fungi. Increased efficacy, chemical stability, non-toxicity, and biocompatibility are the advantages of the biocidal polymers [37]. Of the several biocides, the natural polymer chitosan is well known for its biocidal properties [38]. Poly(propyleneimine) dendrimers [39] and N-halamines [40] are few examples of synthetic biocides.

Superabsorbent Polymers

Superabsorbent polymers are a class of hydrogels to find application in agriculture primarily employed to hold moisture content of the soil. Acrylate-based polymers are used as superabsorbents for a long time. These materials are not biodegradable. Later, cellulose-based superabsorbents developed with easy biodegradability with potential commercial applications in agriculture [41].

4 Degradable Polymers in Personal Care

4.1 Polymer in Personal Care

In this part of the chapter, the use of degradable polymers in personal care is presented. Polymers in personal care must be biocompatible along with the biodegradable properties. Most of the personal care applications have been applied topically over the skin. In topical applications, the skin absorbs active ingredients to produce therapeutic effects. In this case, biocompatibility and biodegradability of the materials are essential to be non-toxic. Later, unabsorbed materials are washed off which eventually accumulates in the environment. The washed off materials must be degraded either by biomechanism or any other degradation means.

Polymers in cosmetic and personal care products function as emulsifiers, modifiers, thickeners, film formers, aesthetic enhancers, and protective barriers. These high-performance products are made of both natural and synthetic polymers. Polymers as thickeners improve the rheology of the formulation while increasing the water sensitivity and delivery of the active component. Vinyl acetate, vinyl pyrrolidone, and modified dimethicones are employed in thickening applications. Further, to improve the viscosity, natural polymers such as polysaccharides, alginates, gelatin, xanthan gum, guar gum, and pectin are used [42].

Alkylene oxide-based homo, copolymers, acrylic acid-based polymers, and polyacrylamide find application in emulsion-based personal care products [43]. In hair

conditioning applications, polymers are used to modify the negative charge of the hair. Mostly cationic polymers such as polysaccharides, natural gums, hydrolyzed proteins, and synthetic polymers such as polyvinylpyrrolidone, polyvinyl acetate, and polyurethanes are used in cosmetic applications. In the nail products, polyurethanes are used as secondary film formers. In the category of active delivery systems in personal care, poly(anhydride-esters) find excellent application [44]. In this class of application, polymers entrap the active components, which enhance the shelf life of the formulation. Polyethylene microbeads find application in personal care products as a scrub. These polyethylene-based microbeads are not readily biodegradable.

4.2 Biodegradable Polymers as Encapsulation Materials

Transdermal and topical cosmetic applications should be biologically safe to ensure efficacy without any side effects. Most of the active components used in cosmetics are sensitive to temperature, oxidation, light, and pH. Polymers play a wide role as an encapsulant to protect active ingredients from the said factors. The encapsulation enhances the efficacy and bioavailability of the active ingredient. Finally, the polymeric carriers are eliminated through the normal metabolic pathways [45].

Polymers such as polylactide (PLA), polyglycolide (PGA), and respective copolymers are synthetic materials used in the transdermal delivery of cosmetics. In the natural polymer category polysaccharides, modified polysaccharides and chitosan are extensively used [46].

Permeability through cells connecting stratum corneum with the epidermis of the skin structure was one of the major challenges faced in achieving transdermal delivery [47] Intercellular and transcellular routes are the possible pathways of drug delivery through the skin apart from hair follicles. Polymer-based permeation enhancers are used to achieve transdermal delivery of active ingredients. Stratum corneum is a lipid-rich matrix. Delivering hydrophilic substances through the lipid-rich environment needs optimum lipophilicity in the formulation [48]. The best possible way to active delivery ingredients through the lipid-rich stratum corneum matrix is by disruption of the cellular structure by either physical means or chemically [49]. Iontophoresis, microneedle arrays, electroporation, and sonophoresis are the physical ways of disrupting the skin structure to improve the permeability [50]. Biodegradable polymers have been employed as chemical permeability enhancers in transdermal delivery of personal care products and cosmetics.

Chitosan is known to enhance permeability through the skin by altering keratin. The presence of glucosamine in chitosan carries a positive charge in slightly acidic conditions which depolarize the negative charge of the cell structure, thereby decreases the overall cell membrane potential. This phenomenon mediates passage of active component through the skin [51, 52]. Successful controlled release transdermal delivery of retinoic acid was achieved after encapsulation with chitosan [53]. After cross-linking and coacervation, less water-soluble retinoic acid encapsulated and delivery through the skin (Chitosphere ™).

Hyaluronic acid, made up of N-acetyl-glucosamine and glucuronic acid, is an anionic natural polysaccharide. It is a topical humectant absorbs water from the atmosphere to keep the skin moisturized. The benzyl ester of hyaluronic acid used as a delivery system to transdermally deliver keratinocyte cells obtained from tissue culture for burn wounds with high healing rates [54]. In a study, hyaluronic acid encapsulated vitamin E used to deliver through the stratum corneum [38]. In tropical applications using hyaluronic acid, the degree of hydration plays a vital role in achieving desired results.

Cyclodextrins, made up of glucopyranose units, is a cyclic oligosaccharide. The cyclic structure is hydrophobic in inner cavities and hydrophilic in outer surfaces. The complex forming abilities of cyclodextrins make this oligosaccharide one of the highly successful materials in cosmetic delivery applications. The improved effectiveness of cyclodextrins in sunscreen formulations is well known [55]. Several skin formulations based on cyclodextrins are commercially available [56].

Excellent complexing abilities of alginates make this polymer a highly used material in cosmetic and personal care applications. Under mild conditions, alginates are used in protein delivery systems with minimal denaturation [56]. US patent 5204111 describes alginate-based capsules for cosmetic applications. Starch–chitosan-based transdermal patches have been reported for skin lightening purposes [57].

Starch and modified starch find multiple applications as thickeners, film formers, and absorbent in cosmetics. This natural polymer widely used in many drug delivery applications. US patent 2010098734 describes a novel method of delivering botanical extracts based on encapsulation. Another application utilizes an encapsulation technique using starch to deliver antioxidant and UV absorbent on the skin [58].

In synthetic biodegradable polymers category poly(lactide-co-glycolide) (PLGA) poly(L-lactide) (PLA), and poly(caprolactone) (PCL), polyglycolide (PGA) dominates in personal care formulations. These polyesters degrade by ester hydrolysis under aqueous conditions and produce lactic acid, glycolic acid as degradation products [59].

In anti-wrinkle treatment, PLA-retinyl retinoate microspheres have been reported, and results confirmed the deep penetration of the active ingredients across the skin layers [60]. In moisturizer applications, PLGA-urea microspheres produced stable and controlled release to provide better results compared with urea alone. Also, the stability of ascorbic acid in cosmetic applications is enhanced by encapsulation with PLGA [61, 62]. In sunscreen applications also, the use of PLGA successfully demonstrated in several studies. Polyalkylcyanoacrylates are another class of synthetic polymers used for encapsulating oil delivery. With the growing demand for high-performance personal care products, in the future, much more tailor-made biodegradable polymers can be developed for the encapsulation of active ingredients.

5 Polymers in Packaging

Packaging applications of polymers are broadly divided into two classes. The first being polymers for food packaging and the second being polymers used in packaging other than food applications. The two classes are based on the basic requirements of packaging. For food products, the requirements are different such as packaging under nitrogen and preservation of moisture. Mechanical, thermal, and barrier properties of polymers play a major role in the packaging applications [63]. One important fact to consider in applications of polymers in packaging is the volume of material involved. In the polymers manufactured throughout the world, about 50% is consumed in packaging applications alone, and the majority of polymers come under the non-biodegradable category (polystyrene, polyethylene). Polymers such as PLA, PHA, chitosan, and several other biodegradable polymers are used in packaging applications. Apart from virgin polymers, polymers reinforced with nanomaterials (polymer nanocomposites) are also used in packaging. Considering the quantum of polymer used and the amount of polymer waste generated in packaging, the paradigm shift toward biodegradable polymers to sustain growth can be understood.

Any packaging is characterized by primary and secondary functions of the material used. Protecting the packaged product during storage, loading and transport are the primary functions, and the physical appearance of the package is the secondary function. Good mechanical properties, resistance to atmospheric conditions, and recyclability are the essential criterions of polymers used in packaging applications [64]. To qualify polymers to meet these requirements, mechanical properties such as tensile strength, tear strength, bursting strength, and impact strength are essential. Thermal properties such as heat capacity, heat of fusion, heat deflection temperature, melting temperature and glass transition temperature, optical properties such as haze, gloss, transparency, and opacity, morphology properties such as crystallinity and degree of crystallinity, barrier properties such as solubility coefficient, diffusion coefficient, and permeability are important.

LDPE and LLDPE are the polymers occupy the place of the highest volume of consumption in packaging applications followed by HDPE. The other high-volume polymers used are polyethylene terephthalate, polyvinyl chloride, polystyrene, and polypropylene. All these polymers are derived from petroleum sources.

Among these polymers, polyethylene is the most commonly used polymer for packaging applications. Polyethylene possesses excellent processability, good electrical insulation properties, easily heat sealable, odor-free, and non-toxic. One of the major drawbacks of polyethylene is poor barrier properties. Oils, gases, and fats easily permeate through this polymer. Non-biodegradability is another disadvantage of this widely used polymer [65]. Polypropylene is another petroleum-derived polymer used in several packaging applications. These polymers are thermally better stable than polyethylene but possess poor oxidative stability. Usually, an antioxidant is added with polypropylene to improve the stability. To improve further, copolymers of ethylene and propylene developed to synthesize polyethylene–polypropylene copolymer to improve properties such as heat stability and oxidative stability [66].

Polyvinyl chloride is a thermoplastic, different from other polymers due to its excellent combustion resistant properties. Properties of PVC can be tailor-made by the addition of additives to improve the tensile strength, toughness, and impact resistance to make it more suitable for packaging applications [67]. Polystyrene is a vinyl polymer. It is an attractive material used in packaging applications for its excellent thermal insulation properties. Foamed polystyrene and expanded finds a special place in packaging applications (widely known generic name as thermocol). Copolymers of polystyrene with butadiene, acrylonitrile, ethylene oxide, and divinylbenzene are well known for the better properties than polystyrene [68].

Polyethylene terephthalate (PET) is synthetic petroleum-based polymer exhibits excellent gas bearing properties and commercially used for packaging of carbonated soft drinks. PET is available in both amorphous and crystalline form which makes the use of the polymer widely used in packaging applications [69].

All the polymers discussed above are non-biodegradable in nature through the applications of these materials are enormous. Usage of these polymers over a long period is a threat to the environment. The need to develop sustainable materials attracted new polymers with degradable properties. Bioplastics such as sugars, proteins, starch, chitosan, and cellulose derived from the natural resources are biodegradable and recycled through nature. Synthetic materials such as poly(trimethylene terephthalate) (PTT) and poly(butylene succinate) (PBS) were developed to meet the requirements of biodegradation. The following review presents the degradable/biodegradable polymer used in packaging applications.

5.1 Degradable Polymers in Packaging

Starch, the biopolymer, is made up of 20–25% amylose and 7–80% amylopectin [70]. Being a semicrystalline polymer, the thermal and mechanical properties of starch are influenced by both crystalline and amorphous regions of the polymer [71]. Main drawbacks of starch in packaging applications are its hydrophilic nature and poor mechanical properties. Usually, by adding appropriate plasticizer the mechanical strength is improved [72]. Hydrophobic nature of starch is improved by the addition of lipophilic materials [73]. The hydrophilic nature of starch makes it easily degradable in the natural environment. Starch molecules are broken by the enzyme amylase produced by Bacillus subtilis, Bacillus licheniformis, Bacillus amyloliquefaciens, and Aspergillus niger. Starch in its unmodified form is degraded in less than six months completely into carbon dioxide and water. In packaging applications, starch alone is used in few applications due to its hydrophilicity and poor mechanical properties. Polymer composites made up of starch and other polymers both of non-degradable/degradable polymers find several packaging applications. Valentina et al. [74] reviewed and reported the complete degradable starch-based composites. PVA, PCL, PLA, and PHA are the major polymers used in preparing the starch-based packaging composites.

The crystalline natural polymer cellulose is insoluble in water and most of the organic solvents. Cellophane is the first cellulose-based commercially successful packaging technology developed. Hydroxyethyl cellulose, Hydroxypropyl cellulose, ethyl cellulose, and cellulose acetate are some of the derivatives of cellulose to find application in the packaging industry. Among the special coating applications of cellulose, the protection of food products is significant. A single layer or multilayer coatings over food products enhance the shelf life of food products. Methyl cellulose and hydroxylpropyl methylcellulose (HPMC) are the two cellulose-based polymers used in edible coating applications.

Chitin, the second largest natural polymer available on earth, is polycationic in nature. Chitin is made up of N-acetylglucosamine and forms the exoskeletons of arthropods. In its pure form, chitin is a tough polymer and also degrades comparatively slowly. These characteristics restrict the large-scale applications of natural chitin. The hydrolyzed product of chitin is chitosan which is a deacetylated polymer that contains free primary amine group in its structure. The presences of a free amine group make the polymer soluble in water under acidic conditions and easily converted to new derivatives. Chitosan is degraded by lysozyme, bacterial enzymes, and chitinases [75]. The major issue in using chitosan in packaging films is its cost. When compared with other natural or synthetic polymers used in packaging applications, cost of chitosan-based films is at least five times higher [76]. Hence, specialized applications such as food packaging where cost is not a barrier employ chitosan-based coatings/films. Among the chitosan-based materials, N,O-carboxymethyl chitosan is known to enhance the shelf life of fruits. In fact, the first granted patent for films based on chitosan was way back in 1936.

Protein-based films adhere to the hydrophilic surfaces than any other polymers. Protein-based films provide a barrier to carbon dioxide and oxygen, but moisture cannot be excluded [77]. Gelatin/Collage, whey protein, casein, fibrinogen, soy protein egg albumin, wheat gluten, and corn zein are examples of protein-based materials used in packaging applications [78]. Almost all the protein-based packaging applications are used as edible films.

Carrageenan, guar, pectins, and alginates are among natural gums which are polysaccharide- based materials used in packaging in particular seafood products [79]. Carrageenan is a mixture of many polysaccharides used in muscle food (fish and poultry-based products) packaging [80].

Polyhydroxyalkanoates (PHA) are natural polyesters produced by bacteria composed of 3-hydroxy fatty acid monomers. Bottles, containers, sheets, films, fibers, and coatings are the packaging applications of PHA. Over a hundred different PHA-based polymers are currently in use. Resistance to water, biodegradability, and thermoprocessability make PHA a preferred choice in food packaging applications [81].

Polylactic acid (PLA) is a readily degradable polymer prepared from the controlled polymerization of lactic acid [82]. Compostability of PLA is well studied, and in the future, this polymer can replace traditional plastics due to its comparative cost and biodegradability [83]. Apart from virgin PLA, polymer blends based on PLA also find applications in several packaging applications.

6 Degradable Polymers in Biomedical Applications

6.1 Bioabsorbable Polymers

Bioabsorbable polymers are a class of specialty materials clinically which serve a function and later on gradually break down, metabolized, and eliminated from the body [84]. The need for bioabsorbable materials mandated from the requirement to eliminate implant removal operations. An ideal bioabsorbable material must have characteristics of design and fabrication according to biomedical requirements such as initial strength, degrade in a predicted way, and biological acceptance. The polymers used in bioabsorbable internal fixation devices predominantly made up of polydioxanone (PDS), polyglyconate, polyglycolic acid (PGA), polylactic acid (PLA), copolymers of PGA-PLA, poly[ortho esters], poly[glycolide-co-trimethylene carbonate], poly[e-caprolactone] (PCL), poly[b-hydroxybutyrate] (PHB), and poly[phbhydroxyvaleric acid]. Among these polymers, PGA is the most crystalline material, but loses all its strength virtually within a month and completely eliminated from the body in 6–12 months [85]. The following table provides the summary of complete absorption and mechanical property loss time of various polymers used in artificial organs.

6.2 Shape-Memory Materials

Shape-memory materials are advanced polymeric materials which undergo a phase transition between an initial temporary phase (a temporary shape) and a permanent phase (a permanent shape) in a biological environment. The shape transition is achieved by changes in body temperature. In general, high transition temperature leads to a permanent shape. Caprolactone and dioxanone-based polymers have been developed for this kind of advanced applications. Mostly shape-memory polymers are developed to function as implants. Most interesting application based on shape-memory polymers being sutures able to self-tie on demand [86].

6.3 Tissue Engineering and Regenerative Medicine

Tissue engineering assembles developed biomaterials to improve damaged tissues or regenerate the whole organs to restore normal physiological function. Construction of porous scaffolds which aids in regenerating the tissues is the foremost objective of tissue engineering research. The tissue engineering technologies use scaffolds in cartilage, bone, ligaments, skin, neural tissues, skeletal muscles, vascular tissues, and artificial skin in regenerative medicine [87]. In regenerative medicine, self-healing of tissues happens by its own systems or with the support of foreign materials to recreate

cells. Both tissue engineering and regenerative medicine aim to cure complex chronic diseases [88].

Direct replacement of tissues being studied using naturally available building blocks which includes extracellular matrixes (ECM). Recombinant DNA technology made it possible to generate ECM composites for biomedical applications [89]. Biocompatible polymeric biomaterials are widely used in tissue engineering in developing technologies to cure diseases. Polymers of synthetic origin such as poly(lactic-co-glycolic) acid (PLGA) and polyanhydrides, naturally occurring polymers such as hyaluronan, chitosan, and hydroxyapatite, are the examples of biomaterials used in tissue engineering. The major advantage of synthetic polymers in developing biomedical technologies is that custom designing of properties such as desired mechanical strength, porosity, and tailor-made degradation time to adapt to the requirements.

6.4 Degradable Polymers in Other Biomedical Applications

For the application as biomaterials, degradation under hydrolytic conditions is essential. The complex aqueous biological environment is the only determinant defines the biodegradation rate, and polymers are custom designed based on this requirement. Polymers such as polyphosphazines, polyacetals, polycarbonates, polyurethanes, polyanhydrides, polyesters, and polyamides are the class of materials capable of degrading under hydrolytic conditions. Among these polymers, polyphosphazines degrade very fast, and polyamides take the longest time. To meet the requirements, copolymers are also attempted [90]. The easy of synthesis, tunable physicochemical properties such as hydrophobicity, the rate of erosion, the rate of degradation, mechanical strength, and inertness make polyesters as one of the highly investigated material in the modern era [91, 92, 93, 94].

Polymers such as PLA, PCL, and PLGA have been used in biomedical applications for the fabrication of sutures, implants, and drug delivery. In particular, for sutures, PGLA and PGA are used extensively [95]. In bone repair applications, PLA has been used due to its superior load bearing capacity than the other polymers [96]. A summary of biomedical applications of some important polyesters is presented in Table 4.

Apart from the above-said synthetic degradable polymers, from the materials of natural origin chitosan has been studied for biomedical applications [97]. Biocompatibility and least toxicity make nature-based polymers very attractive for biomedical applications. Wound healing, drug delivery, bone repair, cartilage tissue engineering, scaffolds, and nanotechnology-based applications are some of the biomedical applications of chitosan-based materials.

Drug delivery applications of degradable polymers have developed to very advanced level. Both natural and synthetic polymers have been studied for technologically advanced applications. Choice of widely available synthetic polymers and definable properties makes the synthetic polymers highly usable in drug delivery. Controlled drug delivery, targeted drug delivery, and solubility enhancement

Table 4 Summary of biomedical applications of some important polyesters

PCL	Vascular grafts, cardiac patches, surgical meshes, stents, and tissue repair [98, 99, 100, 101]
PLGA	Stents, sutures, plates, drug delivery, and tissue engineered vascular grafts [98, 102, 103]
PLA	Vascular grafts, scaffolds, reconstructive surgeries, treatment of fractures [98, 91, 92]
PHB	Nerve repair, wound dressing, stents, hemostats, surgical meshes [98, 103, 104, 105]
PBS	Stents, sterilization wrap, diagnostic imaging [99]
PPF	Orthopedic implants, scaffolds [102, 91, 92]

are the prime importance in polymer-based drug delivery. Among synthetic polymers, poly(L-lactide) (PLLA), poly(D, L-lactide) (PDLLA), and poly(lactide-co-glycolide) (PLGA) are widely used due to the versatile properties of these polymers. Among natural polymers, chitosan is widely used. The drug delivery properties of chitosan entirely depend on its molecular weight. Biodegradable block copolymers are capable of forming micelles useful in drug encapsulation and drug delivery. Block copolymers of PEG (hydrophilic moiety) with PLA, PGA, PLGA, PCL (hydrophobic moiety) forms micelles in enhancing drug delivery.

With the help of conjugation of targeting groups with a suitable polymer, site-specific drug delivery can be achieved. Functionalization of targeting groups plays an important role in this kind of techniques.

7 Conclusions

Advancement in polymer chemistry leads to versatile applications useful in day-to-day life in every possible area in the last century. Of late, it was understood that the volume of waste generated by using these polymers severely affected the environment. To minimize the impact on the environment and to sustain growth, developing biofriendly materials became inevitable.

Degradable materials play a significant role in developing a wide variety of applications in agriculture, personal care, packaging, and biomedical technologies. Improved properties of the degradable polymers either alone or in composition with other materials produced technologically advanced applications. However, the low-volume consumption of degradable polymers due to higher cost and tough preparative methods needs improvement to sustain biofriendly technologies. The present review presented versatile applications of degradable polymers to highlight the significance of these materials.

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Chapter 18
Magnetic Cellulose Green Nanocomposite Adsorbents for the Removal of Heavy Metal Ions in Water/Wastewater

K. Seeni Meera and D. Arunbabu

1 Introduction

The rapid growth of urbanization and industrialization has become one of the pressing issues all over the world, which severely contaminates groundwater and surface water. The pollution of ground and surface water created inadequate access to clean and fresh water for the people. The water shortage and pollution will endanger the life of human beings and many living creatures. In developing and industrialized nations, the discharge of heavy metal ions like Pb^{2+}, Hg^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}, As^{5+}, Cr^{6+} and Cu^{2+} from various industries [21, 62, 66, 65, 69, 90] like metal finishing, semiconductor, batteries, leather, tannery, electroplating, oil, dye and pigment are very important environmental threats to human and aquatic life. The heavy metal contamination limits the availability of drinking water and causes severe health problems like kidney and liver damage, which creates mutagenic and carcinogenic effects to human beings [50, 51, 76]. Therefore, it is important and essential to remove heavy metal ions from water/wastewater solution. There are several methods available for the removal of toxic heavy metal ions from water/wastewater such as adsorption, ion-exchange, coagulation, chemical precipitation, electrodialysis, oxidation, ultrasonication, flocculation, membrane filtration, sedimentation, electrochemical oxidation, and cementation [38, 47, 52, 53, 65, 64, 63]. Among all the methods mentioned above, adsorption is an easy, simple, low cost, and highly effective method for the removal of heavy metal ions from water/wastewater solution [28]. Numerous adsor-

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bents were developed for the removal of heavy metal ions from water/wastewater such as activated carbon, zeolites, clay minerals, agricultural wastes and low-cost adsorbents from easily available polysaccharides, namely cellulose, chitosan, chitin, alginate and their derivatives [19, 39, 44, 68]. The requirement of adsorbents from an eco-friendly material (polysaccharide) is to reduce the treatment cost and also to avoid hazardous by-product formation at the end of the treatment process. Moreover, polysaccharides have excellent characteristics like particular structure, excellent chemical stability, high reactivity, affinity, and selectivity toward heavy metal ions and aromatic compounds due to the presence of various functional groups on its surface such as hydroxyl, amino, or acetamido [19]. Among various polysaccharides, cellulose is one of the most important and abundant green biopolymer, which showed numerous applications to mankind due to its bio-renewable, biocompatible, and biodegradable nature. Cellulose-based adsorbents play a vital role in removing various toxic pollutants such as heavy metal ions, dyes, oil, pesticides, and radioactive metals from water/wastewater solution [4, 5, 59, 91]. Although cellulose-based adsorbents are difficult to separate from wastewater at the end of the treatment process, it can be separated only by filtration or centrifugation at the end. The conventional cellulose-based adsorbents are limited by their low adsorption capacity and separation difficulties [103]. Therefore, there is a demand and necessity to develop an adsorbent system with good adsorption capacity, efficiency, and easy separation are of current interest among all the researchers throughout the world.

To overcome the above hurdles, magnetic adsorbents have been proposed as a suitable material for the removal of heavy metal ions from water/wastewater solution. Magnetic adsorbents are a new class of materials find an important place in water treatment due to their very good adsorption efficiency, low cost, rapid separation, low production of contaminants, and large quantity of treatment within short operation time [55, 78, 96]. In addition, green biopolymer cellulose-based adsorbents are interesting materials, which can be easily adsorbed on the surface of inorganic magnetic nanoparticles (Fe_2O_3/Fe_3O_4) [6, 48]. Moreover, cellulose contains a large number of hydroxyl groups on its surface, which can be strongly interacted with inorganic particles through strong *van der Waals* interaction [103]. These superior properties of cellulose made them as a promising candidate for preparing magnetic adsorbent materials in different forms such as hydrogels, aerogels, and beads [55, 78, 96]. These magnetic materials can easily respond to the external magnetic field, which made them interesting magnetic responsive materials for various applications in environmental remediation, sensor, biomedical, and diagnostic fields [43]. The development of an efficient adsorbent system mainly lies in the direction of low-cost adsorbent with magnetic separation due to its amazing separation speed [67, 11, 34, 41, 54, 79]. Therefore, development of cellulose-based magnetic materials provides a new insight into the perspective of removing toxic heavy metal ions from water/wastewater solution.

2 Cellulosic Bead Adsorbents

Cellulosic materials are formed by the dissolution, shaping, and regeneration of cellulose fiber powder. The regeneration of the cellulose solution as microbeads is shown in Fig. 1. They are spherical beads (diameter $\geq$ 10 μm) constitute cellulose with re-establishment of hydrogen bonding interactions [30, 40]. Cellulose beads were developed by the dissolution in 8 wt% NaOH, shaping followed by supercritical drying under CO_2. Further, inorganic particles (like Iron, TiO_2, carbon black, and copper powder) were encapsulated into the beads to provide the evidence of its encapsulation efficiency [60, 75]. Cellulose beads have been developed by different approaches, viz. dropping [10], viscose-phase separation method [56], double emulsification process [27, 85], periodate oxidation of cellulose [45], spray-freeze-drying [13], etc. As already mentioned above, cellulose bead formation achieved by the dissolution of cellulose in a variety of solvents. The different solvents available in the literature for the dissolution of cellulose are tremendous and name a few, NaOH/urea [87], LiCl/DMAc [15], H_3PO_4 [35], ionic liquids [83, 106], N-methyl morpholine-N-oxide (NMMO) [29], inorganic molten salts ($Ca(SCN)_2{\cdot}4H_2O$ and $ZnCl_2$) [42, 72], etc. In addition to cellulose dissolution and its shaping, regeneration of cellulose is also an important process in forming beads. The most commonly employed regeneration fluids are H_2SO_4, aq. $CaCl_2$ solution, HCl, $FeCl_3$ solution, ultrapure water, etc. [92, 95, 105].

Owing to its importance and easy process, the potential uses of cellulose beads in various fields are tremendous. Predominantly, cellulose microbeads have potential application in water/wastewater treatment field as an adsorbent for metal contaminants and stabilizer for active pollutants [14, 33]. The reason behind the potential use of green biopolymer cellulose in water treatment mainly due to the following factors:

(i) The crystalline regions have length and a lateral dimension of 200 and 5 nm, respectively. The advantages of having smaller dimension results in higher aspect ratio (L/d), which gives a high surface area [97].

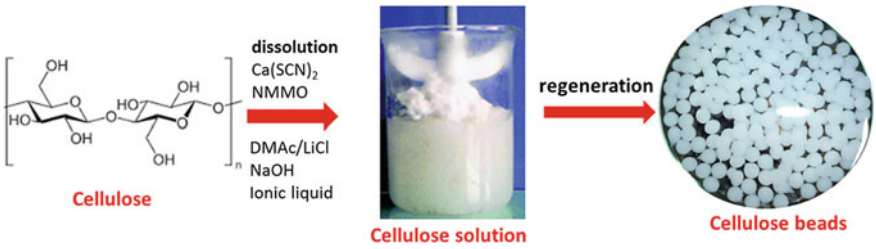


Fig. 1 Simple schematic representation of cellulose bead formation [61, 40]

(ii) Cellulose contains a large number of hydroxyl groups on its surface. Due to this, cellulose exhibits high activity and ability to bind with heavy metal ions such as Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} and Cr^{6+}[57, 71, 88, 102].

It has been demonstrated that precipitation polymerization technique could be used to prepare composite beads of sugarcane molasses with cellulose and utilized them for treating dye polluted wastewater [7]. An interesting example [89] of biopolymeric composite beads that containing cellulose/chitosan/alginate were used for the treatment of Cu^{2+} ions from an aqueous solution. A series of studies pertaining its influence over Cu^{2+} ion removal as a function of adsorbent dosage, pH, contact time, and metal ion concentration was well demonstrated [89]. The combination of carboxymethyl cellulose and alginate was used to produce bead form, which demonstrated very good adsorption toward As^{5+} metal ions and its adsorption efficiency can be tuned by altering pH and ionic strength of As^{5+} solution [86]. In another example, the ionic gelation technique was employed to develop calcium alginate-carboxymethyl cellulose beads by interacting with Ca^{2+} ions [1]. An excellent mercury adsorbent was developed by Dewangan et al. [23] from carboxymethyl cellulose and alginate in the form of beads. The maximum mercury adsorption was found at pH 6.0 within a very short contact time of 60 min. Moreover, the adsorption is more dependent with respect to the contact time and ion concentrations.

2.1 Mechanism of Cellulose Binding with Heavy Metal Ions

The binding of green biopolymer cellulose with heavy metal ions can take place via three different mechanisms:

(i) sorption [both absorption and adsorption],
(ii) electrostatic interaction [in the absence of ligand], and
(iii) electrostatic interaction [in the presence of ligand] [97].

The surface of cellulose fiber solution carries negative charge due to the presence of protolytic carboxylic (≡COOH) and phenolic (≡OH) groups. The surface charge of cellulose fiber solution under different pH is shown below [88]:

$$-\mathrm{COOH} \rightleftharpoons -\mathrm{COO}^- + \mathrm{H}^+ [\text{under neutral or acidic pH}] \quad (1)$$

$$-\mathrm{OH} \rightleftharpoons -\mathrm{O}^- + \mathrm{H}^+ [\text{under alkaline pH}] \quad (2)$$

The positively charged metal ions interact with negatively charged cellulose adsorbent (Eqs. 1 and 2), thereby adsorption takes place. However, the unmodified cellulose adsorbent shows low metal adsorption capacity and different physical stability [57]. Therefore, modification of cellulose adsorbent is an essential factor to achieve suitable structural stability and efficient adsorption capacity for different heavy metal ions [33].

3 The Magnetization of Cellulose Adsorbents

The modification of cellulose adsorbent by means of magnetic assistance [3, 22, 49, 58, 60] attracted several researchers during the recent years. The magnetization of adsorbents plays a vital role in water purification, which directly influences the physical properties of toxic pollutants.

3.1 Surface Modification with Fe_3O_4 Nanoparticles

The most commonly used magnetic material is Fe_3O_4 nanoparticle (magnetite) because of its superior properties like easy preparation, low cost, easy compatibility, and good magnetic property [71]. The incorporation of magnetic nanoparticles into cellulose solution eliminates the chances of forming aggregates due to its dipolar interactions [102]. In an aqueous solution, the surface of Fe_3O_4 covered with FeOH, which exists as $FeOH_2^+$ or FeO^- on the surface at below or above its pH_{pzc} of 7.4 (point of zero charges) [2].

$$FeOH + H^+ \rightleftharpoons FeOH_2^+ [\text{under acidic pH}] \tag{3}$$

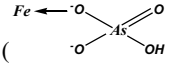
$$FeOH + OH^- \rightleftharpoons FeO^- + H_2O \text{ [under alkaline pH]} \tag{4}$$

The adsorption occurs mainly based on the electrostatic attraction between metal ion species and the surface charge of Fe_3O_4 nanoparticles depending upon the pH of the solution. In basic pH, strong attraction exhibited between negatively charged surfaces of the adsorbent (FeO^-) and positively charged metal ions. However, the decrease of pH changes the electrostatic interaction between metal ions and the positive charged surface of the adsorbent ($FeOH_2^+$) [strong repulsion exists] thereby adsorption efficiency decreases.

The magnetic response of a specific metal ion is largely depending on its magnetic susceptibility (χ). Further, adsorption of the metal ion by magnetite adsorbent is more ions specific with respect to the pH of the solution. Magnetite (Fe_3O_4) nanoparticles showed excellent adsorption capacity of 53.11 mg/g for Pb^{2+} ions at pH 5.0 (45 °C) [37, 50, 51]. The adsorption mechanism of Pb^{2+} with the Fe_3O_4 adsorbent is as follows: In an aqueous condition, Pb^{2+} exist in different forms such as $Pb(OH)_2$ (pH > 6.5) and Pb^{2+} and $Pb(OH)^+$ (pH < 6.5) [98]. The adsorption occurred via electrostatic interaction between FeO^- and Pb^{2+} with increasing pH (increasing pH creates large repulsion between $FeOH_2^+$ and Pb^{2+}). Therefore, the adsorption efficiency of Fe_3O_4 toward Pb^{2+} is high at or above pH 5.0 [37].

The same author [37] observed maximum adsorption of Cr^{6+} (34.9 mg/g) at pH 2.0 (45 °C). Cr^{6+} ion exists as different species in acidic solution as, $HCrO_4^-$, $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$, and $Cr_4O_{13}^{2-}$. The adsorption free energy (ΔG_f^0) of $HCrO_4^-$ is lower than that of other species at pH 2.0. Hence, the adsorption of Cr^{6+} with Fe_3O_4 is most

favorable at lower pH. The increase of pH decreases the adsorption of Cr^{6+} by Fe_3O_4 due to increase in the concentration of OH^- ions (competition exists between OH^- ions and Cr^{6+} species in CrO_4^{2-} for the adsorption sites). Fe_3O_4-based adsorbent showed an excellent affinity toward adsorption of heavy metal ions specifically Pb^{2+} and Cr^{6+}[37].

In addition, iron oxide adsorbed strongly with toxic heavy metal ions like As^{5+} and Cr^{6+} (which exists as $HAsO_4^{2-}$ and CrO_4^{2-}, respectively) [100] because of their strong complex formation  with Fe_3O_4. In acidic pH 5.0, As^{5+} predominantly present as $H_2AsO_4^-$ and $HAsO_4^{2-}$ whereas As^{3+} present as $H_3AsO_3^0$ (nonionic form) [17, 46]. The selective adsorption of As^{5+} facilitated through interaction between negatively charged As^{5+} species ($H_2AsO_4^-$ and $HAsO_4^{2-}$) and positively charged Fe_3O_4 nanoparticles ($FeOH_2^+$). So, the adsorption of As^{5+} by Fe_3O_4 surface is more pH-dependent and strong adsorption exists in acidic pH [46].

In an approach, the solution polymerization technique was employed to develop ferric oxide embedded porous cellulose bead using a simple strategy with low energy consumption. The synthesized porous beads exhibit a high uptake of toxic Hg^{2+} ions (pH 6.0) with a load of 10 wt% of ferric oxide [31]. The very interesting study focused on the removal of highly toxic and radioactive U^{6+} ions through nano-Fe_2O_3 impregnated cellulose beads [70]. The impregnation of nano-Fe_2O_3 inside cellulose provides superior advantages such as stability of nanoparticles, increased adsorption capacity due to various cellulosic functionalities, and good porosity for efficient adsorption of U^{6+} ions [70]. The modification of cellulose bead with metal ions like Ce, Al, and Fe provided more selective adsorption toward As^{5+} ions from drinking water. The adsorption of $As^{5+}$is significantly depended on the pH of the system, especially at acidic pH of 3.0, maximum adsorption efficiency was achieved. A simple methodology has been developed for preparing magnetic cellulose beads through precipitation technique by impregnating Fe_2O_3 onto cellulose acetate beads. It has been utilized for the removal of As^{5+} ions from an aqueous solution. The removal of As^{5+} over 65% was achieved within 4 h, and it can be reused for five consecutive cycles [77].

3.2 *Surface Modification with Fe_3O_4@SiO_2 Nanoparticles*

On the other hand, Fe_3O_4 nanoparticles have the tendency to aggregate because of their self-interactions, which limits their adsorption behavior to certain metal ions. To strengthen its adsorption behavior and prevent aggregation, the surface of Fe_3O_4 nanoparticles was coated with a different metallic layer such as Si, Ag, and Au [8, 93]. Silica (SiO_2) coating on the surface of the Fe_3O_4 nanoparticle is more important because SiO_2 is an excellent surface modifier [24]. Moreover, silica has exceptional biocompatibility, stability, and less toxicity. Further, it can be easily coupled with different functionalities thereby selectivity and specificity could be achieved. The

protonation/deprotonation of SiOH groups on the surface of SiO_2 nanoparticle creates a charge on the surface as given below [9, 16, 94, 101].

$$SiOH + H^+ \rightleftharpoons SiOH_2^+ \text{[under acidic pH]} \quad (5)$$

$$SiOH + OH^- \rightleftharpoons SiO^- + H_2O \text{ [under alkaline pH]} \quad (6)$$

According to [94], under acidic condition Hg^{2+} exists in anionic form $HgCl_3^-$ or $HgCl_4^{2-}$. Hence, the adsorption of Hg^{2+} under acidic pH is very less whereas increase in pH of the solution results in the decrease of anionic form of Hg^{2+}. The interaction between negatively charged adsorbent (SiO^-) and positively charged metal ion (Hg^{2+}) is predominant at pH 6.0 and remains constant above pH 6.0. In a similar fashion, Cu^{2+} ions can be adsorbed on the surface of silanol groups at pH 3.0. The Cu^{2+} adsorption by $Fe_3O_4@SiO_2$ will increase with increasing pH because of the formation of more negatively charged SiO^- species, which strongly interact with Cu^{2+} ions [16].

3.3 *Surface Modification with $Fe_3O_4@SiO_2@Ag$ Nanoparticles*

Moreover, surface of Fe_3O_4 nanoparticles can be also coated with Ag nanoparticles, which can form dimer nanocomposites and possess dual role of magnetic and catalytic functions toward toxic contaminates [32, 73, 74, 80]. However, for the protection of Fe_3O_4, immobilization of Ag and also to avoid the aggregation of Ag nanoparticles, a layer of silica can be formed over Fe_3O_4 [26]. The mechanism of immobilizing Ag nanoparticle over the surface of silica coated Fe_3O_4 is shown below [99].

According to Eq. 6, SiOH exists as SiO^- under alkaline condition. Then, binding of Ag^+ with SiO^- will be achieved through electrostatic attraction (Eq. 7) followed by the reduction of Ag^+.

$$SiO^- + Ag^+ \rightarrow Si - O - Ag \quad (7)$$

This resulted in the immobilization of Ag nanoparticles over the surface of silica coated Fe_3O_4 nanoparticles as depicted in Fig. 2 [99].

In general, $SiO_2@Ag$ show excellent surface plasma resonance (SPR) compared to Ag nanoparticles alone. Therefore, the detection of heavy metal ions such as Pb^{2+}, Cd^{2+}, and Zn^{2+} was achieved using silver embedded adsorbents with a size of 220 nm (shell thickness ≈20 nm) [84]. Several studies on the interaction of Ag with heavy metal ions such as Cd^{2+}, Ni^{2+}, and Hg^{2+} have been extensively studied [20, 36, 81, 12].

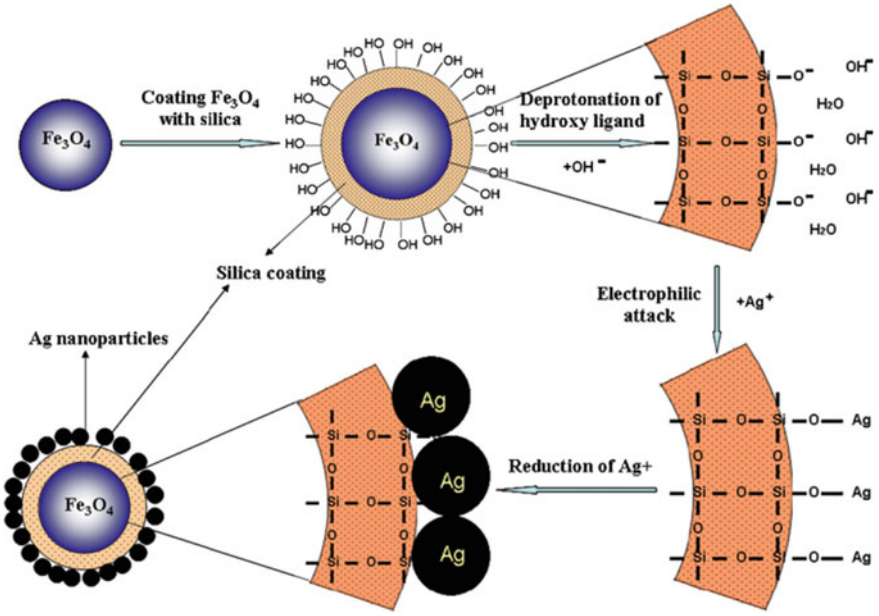


Fig. 2 Schematic representation of Ag binding over the surface of silica coated Fe_3O_4 nanoparticles [99]

3.4 Magnetic Cellulose Beads as Adsorbent Material

Based on the merits and advantages of green biopolymer cellulose, Fe_3O_4 and selective metal nanoparticles (Si and Ag), the present chapter focused on the development of magnetic cellulose aerogel microbead adsorbents. The modification of cellulose adsorbent with magnetic counterpart and its surface coating may provide exceptional specific metal adsorption capacity as well as multiple metal ions (multiple pollutants) [100] from water/wastewater solution. Few studies reported in the literature on the use of Fe_3O_4 embedded cellulose aerogel beads and their coating with metal nanoparticles. Some of the reported results were discussed below:

The magnetic response and high efficient removal of Cu^{2+}, Pb^{2+}, and Zn^{2+} ions were achieved by Fe_3O_4 decorated cellulose beads [50]. An attempt has been made by [96] to develop porous cellulose beads through one pot wet extrusion by in situ deposition of $CoFe_2O_4$ particles. The encapsulated $CoFe_2O_4$ particles can provide good adsorption capacity toward As^{5+} and Pb^{2+} ions. An attempt [69] has been made to develop carboxymethyl cellulose beads blended with sodium alginate through cross-linking and beading in $CaCl_2$ and $FeCl_3$ solution. The static adsorption experiments evidenced that the prepared beads could adsorb Pb^{2+} around 99% under optimized conditions [69]. In another approach, a new kind of magnetic cellulose microspheres was obtained by in situ synthesis of Fe_3O_4 nanoparticles inside the pores of cellulose that act as micro-reaction chambers, where oxidation of metal ions occur yield-

ing Fe_3O_4 particles. These microchambers could control the size and shape of the nanoparticles, which helps to achieve good adsorption capabilities [52]. An example of cellulose bead synthesis demonstrated that the embedding of superparamagnetic iron nanoparticles from a solution containing Fe^{2+} and Fe^{3+} solution by an inverse w/o emulsion technique [18]. A new approach has been made to prepare maghemite (γ-Fe_2O_3) particles through submerged circulation impinging stream reactor. Further, Fe_2O_3 blended with cellulose to obtain micrometer-sized magnetic beads. The magnetization of cellulose imparts good magnetic sensitivity, which helps to achieve good desirability toward the removal of dyes and hazardous materials [52]. A different approach [25] has been developed to obtain nano-magnetic cellulose beads through precipitation of cellulose in a mixture containing Fe^{2+} and Fe^{3+} mixture and further grafted with amino groups on the surface. This novel cellulose bead showed a good tendency toward the removal of Hg^{2+}, Cu^{2+} and Ag^{+} ions. The maximum adsorption capacity of 2, 1.5, and 1.2 mmol/g for Hg^{2+}, Cu^{2+}, and Ag^{+}, respectively, was achieved [25]. In another interesting way [82], amine functionalized magnetic cellulose adsorbent was developed by magnetizing silica particles using Fe_3O_4 followed by coating with cellulose dope. The amine functionalization of cellulose surface was done by using grafting of glycidyl methacrylate with ethylenediamine. This new class of magnetic adsorbent had a high uptake of 171.5 mg/g at 25 °C (pH 2.0) toward Cr^{6+} ions with good reusability [82]. An interesting study [104] based on the development of magnetic cellulose adsorbent containing nanoscale zero-valent iron Fe(0) exhibits a very good magnetic response and superparamagnetic property. The as-prepared magnetic adsorbent showed promising adsorption performance toward the removal of As^{3+} ions from solution with the highest removal efficiency of 99.27% (pH 8.0) [104].

Some efforts have been done in the development of magnetic cellulose-based adsorbents specifically in the form of beads. The utility of these adsorbent has been demonstrated in different fields ranging from dye removal, metal ion capture, drug delivery, and protein binding. However, more insight into the development of magnetic cellulose bead is still challengeable among researchers regarding the binding and removal of specific and multi-heavy metal ions present in water/wastewater solution.

4 Conclusion

A range of studies has been done among researchers for the removal of heavy metal ions using low-cost adsorbent materials. But, still, there are more open challenges that need to be addressed. Green biopolymer-based adsorbents can be used for the removal of pollutants, separation of valuable metals, and for analytical purposes for solid phase extraction. The best way to address all the hurdles pertaining in heavy metal ion removal is the development of more specific and efficient adsorbent system having a magnetic response at low cost, *i.e.*, magnetic cellulose aerogel microbeads. Most of the studies investigated for the adsorption of heavy metal ions is mainly using

batch experiments, so packed bed column technique would be an excellent method to find its industrial importance for practical utility. Moreover, magnetic adsorbents have the large surface area and can be easily functionalized. Further, their location and transport in treating a large volume of contaminants could be controlled by applying an external magnetic field. These magnetic adsorbents are pH-dependent and their regeneration could be achieved by slightly changing pH of the solution and/or adding very low levels of acids or bases. This will help us to utilize the adsorbents for several cycles of adsorption and desorption, which can minimize the cost of the process. Moreover, the multidimensional aspects of the magnetic bead adsorbents need to be addressed. Since the contaminated water not only contains heavy metal ions but also contains oil and bacterial impurities. Moreover, it is important to extend detailed studies on the adsorption of multi-pollutant solutions (metal and dye, organic pollutants and metal, organic pollutants and dye) using the proposed magnetic bead adsorbents. The possibility of utilizing magnetic adsorbents as immobilization support carriers in biosensors and bio-sorbents need to be analyzed.

Nowadays, environmental restrictions are increased interests among societies and countries for keeping better environment. Especially, there is an increasing interest in industries toward the use of renewable resources in the research and development sector. The use of polysaccharide derivatives is one among the basic material received considerable attention in water/wastewater treatment. These types of adsorbents based on renewable sources have a great impact on the environmental concern due to their potential for removing hazardous metals causing health problems for human beings. Moreover, the high cost of conventional adsorbents made polysaccharide-based materials as one of the most attractive adsorbents for water/wastewater treatment. In the aspect of water/wastewater treatment, using the low toxic substance and magnetic assistance based easy separation will provide long-term benefits. Cellulose microbeads embedded with metallic nanoparticles will give an edge over commercially available adsorbents. The studies on magnetic cellulose adsorbents will open a new pathway in the development of magnetic adsorbents from other polysaccharides like chitosan and chitin.

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