

Springer Series on Polymer and Composite Materials

Ashok Kumar Nadda
Swati Sharma
Rajeev Bhat *Editors*

Biopolymers

Recent Updates, Challenges and
Opportunities

 Springer

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Preface

The present book *Biopolymers from wastes and by-products: Challenges and opportunities* is designed with an innovative approach and is motivated by the avenue to explore new strategies for valuable resource recovery from industrial wastes and its further use for mankind. The remarkable developments in industrialization and urbanization across the world have resulted in an imbalance in our ecosystem. Of late, numerous synthetic polymers, chemicals, pesticides, fertilizers, drugs, pharmaceuticals, plastics and synthetic biocides have considerably created an imbalance in the environment, thus creating enormous stress. Synthetic plastic paints, varnishes, plastic-based furniture and automobile coatings are some of the common commodities used in our day-to-day life. It is a known fact that we need to synthesize and use a wide array of synthetic materials for day-to-day usage and discard it afterwards. But, what should be the fate of the remaining wastes or how zero waste concepts could be developed is still a major challenge to be resolved by the scientific community, including the environmentalists. Of course, energy and resource recovery from the generated waste can be of help up to a certain extent to reduce the excess load of wastes and up-cycling them. Waste materials generated as a result of human practices and interventions contain huge amounts of biopolymeric materials. In today's global scenario, the application of appropriate green technologies for effective valorization of wastes presume much importance.

Biopolymers naturally occur as polymeric biomolecules and treasure lots of potential applications as food packaging materials, thin wraps, tissue-engineering material and much more. Furthermore, naturally synthesized biopolymers are non-toxic and are easily biodegradable. The biopolymers extracted from the waste biomass/by-products from industry can be reused in many of the potential applications. However, the production and extraction of biopolymers from wastes necessitate the need for more sustainable approaches. In addition, the re-entry of biopolymers and their composites into the human supply chain should be in such a way that they do not disturb the natural biodiversity or create an imbalance in nature. Besides, effective use of wastes can ensure a sustainable approach to support the circular economy of a region.

This book emphasizes mainly on the extraction, formulations, modification techniques, challenges and opportunities of biopolymers obtained from industrial wastes, and thereby identifying their potential applications in various fields. In particular, the rationale of this book is to provide a compiled monograph from which industrialists, researchers, students and academicians working in the field of waste management will get access to updated knowledge and recent developments in the field. In the book, the first chapter describes the basic introduction of biopolymers present in the waste biomass and briefly highlights on the extraction strategies. The second chapter deals with the importance of bio-based polymers, fabricated or degraded naturally, their classification, applications and biological activities. Chapters “[Biopolymers: Global Carbon Footprint and Climate Change](#)”–“[Sustainable Green Methods for the Extraction of Biopolymers](#)” deal with providing an overview of the polyhydroxyalkanoates and polylactic acids and cover those aspects relevant to the carbon footprint and climate change. In these chapters, recent developments, biodegradability, compostability and applications of various biopolymers have been discussed. In chapters “[Biopolymers from Agriculture Wastes and By-products](#)”–“[Biopolymers from Microbial Flora](#)”, the biopolymers obtained from agriculture, industrial waste and microbial flora have been discussed. In chapters “[The Scope of Biopolymers in Food Industry](#)” and “[Potential Applications of Biopolymers in Fisheries Industry](#)” critical discussions are made on various applications of renewable biopolymers in the food industries and commercial aspects of the seafood industry. Further, different properties of biopolymers from animal, plant and microbial origin to develop the basic raw materials for use in cosmetics, pharmaceutical, biomedical and leather industries have been discussed in chapters “[Biopolymers in Cosmetics, Pharmaceutical, and Biomedical Applications](#)”–“[Biopolymers in Automotive Industry](#)”. The biopolymers in electronics, production of bioplastics and wastewater treatment have been deliberated in chapters “[Biopolymers in Electronics](#)”–“[Bioplastics from Biomass](#)”. Finally, chapters “[Sustainability Challenges and Future Perspectives of Biopolymer](#)” and “[Biomaterials in Coating Industries](#)” summarize the research findings over the recent years and these chapters have been designed to identify various challenges, gaps and future perspectives to overcome the limitations of employing biopolymers in the day-to-day life of humans.

We the editors thank all the authors for their valuable contribution. Further, the editors are thankful to Prof. Susheel Kalia for his valuable inputs and ideas during the compilation of this book. Dr. Ashok Kumar Nadda is thankful to Mr. Sudesh Kumar Mokhta (IAS) Director of Department of Science and Technology (DEST), Government of Himachal Pradesh, India, for his thoughtful ideas and continuous encouragement. In addition, Prof. Rajeev Bhat acknowledges the encouragement received from his University, specifically from Prof (s). Ülke Jaakma, Vice-Rector for Research and Toomas Tuiras, Director of Institute of Veterinary Medicine &

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Waknaghat, India
Mohali, India
Tartu, Estonia
December 2021

Ashok Kumar Nadda
Swati Sharma
Rajeev Bhat

Contents

Transforming Wastes into High Value-Added Products: An Introduction	1
Shreya Gupta, Ashok Kumar Nadda, Arun Gupta, Jasdeep Singh, Sikandar I. Mulla, and Swati Sharma	
Biopolymers and Environment	19
Siddappa Kakkalameli, Azharuddin B. Daphedar, Basheerabegum Faniband, Swati Sharma, Ashok Kumar Nadda, Luiz Fernando R. Ferreira, Muhammad Bilal, Juliana Heloisa Pinê Américo-Pinheiro, and Sikandar I. Mulla	
Biopolymers: Global Carbon Footprint and Climate Change	35
Dimitrie Stoica, Petru Alexe, Angela Stela Ivan, Dana Iulia Moraru, Claudia Veronica Ungureanu, Silvius Stanciu, and Maricica Stoica	
Biopolymers: Regulatory and Legislative Issues	55
Maricica Stoica, Dimitrie Stoica, Angela Stela Ivan, and Carmelia Mariana Bălănică Dragomir	
Sustainable Green Methods for the Extraction of Biopolymers	73
Tarun Kumar Kumawat, Varsha Kumawat, Swati Sharma, Vishnu Sharma, Anjali Pandit, Nirat Kandwani, and Manish Biyani	
Biopolymers from Agriculture Waste and By-Products	111
Magdalena Mikus and Sabina Galus	
Biopolymers from Industrial Waste	129
Ankita Vinayak, Swati Sharma, and Gajendra B. Singh	
Biopolymers from Microbial Flora	151
Rani Padmini Velamakanni, B. Shanti Sree, Priyanka Vuppugalla, Rani Samyuktha Velamakanni, and Ramchander Merugu	

The Scope of Biopolymers in Food Industry	173
Shreya Gupta, Anujit Ghosal, Ayanava Goswami, Bhawana, Ashok Kumar Nadda, and Swati Sharma	
Potential Applications of Biopolymers in Fisheries Industry	199
Meenakshi Singh, Krupa Unadkat, Sahil Kapoor, Manoj Kumar Enamala, Punita Parikh, and K. Chandrasekhar	
Biopolymers in Cosmetics, Pharmaceutical, and Biomedical Applications	223
Sneha S. Rao, Athmika, and P. D. Rekha	
Biopolymers in the Leather Industry	245
Ana Maria Mazotto	
Biopolymers in Automotive Industry	271
Zahra Ranjbar, Behnaz Ranjbar, and Sahar Foroughirad	
Biopolymers in Electronics	289
Muhammad Ghozali, Evi Triwulandari, and Witta Kartika Restu	
Biopolymer in Wastewater Treatment	323
Jasdeep Singh, Shubham Kumar, and Swati Sharma	
Bioplastics from Biomass	353
Dimitrie Stoica, Petru Alexe, Angela Stela Ivan, Silviu Stanciu, Daiana Maria Tatu, and Maricica Stoica	
Sustainability Challenges and Future Perspectives of Biopolymer	373
Nur Hashimah Alias, Norfadhilatuladha Abdullah, Nur Hidayati Othman, Fauziah Marpani, Muzakkir Mohammad Zainol, and Muhammad Shafiq Mat Shayuti	
Biomaterials in Coating Industries	391
Zahra Ranjbar and Behnaz Ranjbar	

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Transforming Wastes into High Value-Added Products: An Introduction



Shreya Gupta, Ashok Kumar Nadda, Arun Gupta, Jasdeep Singh, Sikandar I. Mulla, and Swati Sharma

Abstract Waste from various industries and human activities harms the environment, it is being accumulated rapidly due to its slow and improper management. Disposal of waste in landfills is a threat to the environment. Research interest in waste streams valorization is stimulated because of the disposal problems. Researchers are focusing on transforming the waste into useful products as it will help in waste management and also it will help in reducing environmental pollution. Waste from food industries is a reservoir of complex proteins, lipids, carbohydrates and can be used as raw material for the production of valuable metabolites. Such waste can be transformed into various high-value-added products such as biofuels, enzymes, biopolymers, biochemicals, and many other molecules. For the production of biopolymers, waste from many industries such as agriculture, dairy, meat, and seafood have great potential as primary and secondary feedstocks. Although for biomaterials production, different types of wastes can be used as substrates, currently, agro-industrial wastes are gaining more attention as it has a high rate of production worldwide. As global environmental pollution is increasing day by day due to synthetic plastics production, it has become essential to develop bio-based polymers. The biopolymers production from inexhaustible resources and microbial synthesis are facile, scalable, and are comparatively more eco-friendly than chemical synthesis methods that depend upon acid and alkali treatment or blending of co-polymer. In this

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review, we have discussed the transformation of waste into biopolymers, technologies for extraction and production, and their further applications.

Keywords Waste · Biopolymers · Biomass · Agro-industrial · Renewable · Transformation · Applications

1 Introduction

The global population is increasing at an alarming rate. To fulfill the needs of society, there is a huge demand for energy and food which results in increased food processing wastes. According to Food and agriculture organization, approximately one-third of the food produced in the world goes waste which includes approx. 45% of all fruits and vegetables, 35% of all seafood and fish, 30% of all cereals, 20% of all dairy products, 20% of all meat and poultry [16]. In the life cycle of food at every step, there is a loss of food from the production stage to final household consumption. Households, shops, and supermarkets throw away around 35% of the wasted food. In India, around 67 million tons of food are wasted every year. According to the Food Waste Index Report 2021, in India household waste is around 50 kg per capita per year. Waste from the food industry results from the preparation, production, and consumption of food. Wasted food goes to landfill sites and generates harmful greenhouse gases [89]. There are many reasons which cause the wastage of food materials such as acceleration in food demand, spoilage of food before reaching consumers, global trading, etc. The Wastes and Resources Action Programme (WRAP) divided wasted food into three categories: avoidable (apples, slices of bread, meat), possibly avoidable (bread crusts, potato skins), and unavoidable (tea bags, eggshells, meat bones). Composting, landfills, and incineration are some methods to dispose of food waste. Researchers are focusing on developing innovative/new methods to get rid of waste. To overcome many issues such as pollution, economy, and to increase energy conservation, new policies and methods are being introduced for handling and treatment of waste. There is no doubt that food waste is harmful to the environment and it also has some hazardous effects but these can be converted into high-value products or after biological treatment, it can be used as fodder/feed, or in some industries, it can be used as raw material. Food waste can be converted into many products such as enzymes, biofuels, chemicals, bioactive compounds, biopolymers, etc. Figure 1 shows various commercial products that can be produced from food waste. Biopolymers are attracting more attention because of their bio-based nature, biocompatibility, biodegradability [127]. Food waste generated biopolymers can be used for many applications such as in food industries, industrial plastics, cosmetics, medicine, pharmaceutical, water treatment chemicals, clothing fabrics [101]. Due to the poor mechanical, barrier, and thermal properties of the biopolymers, they have limited industrial applications at a large scale [131]. More attention or study is required for using wasted material as useful bioresources. For biodegradable plastics, polyhydroxyalkanoates (PHA) and polylactic acid (PLA) are the main biopolymers.

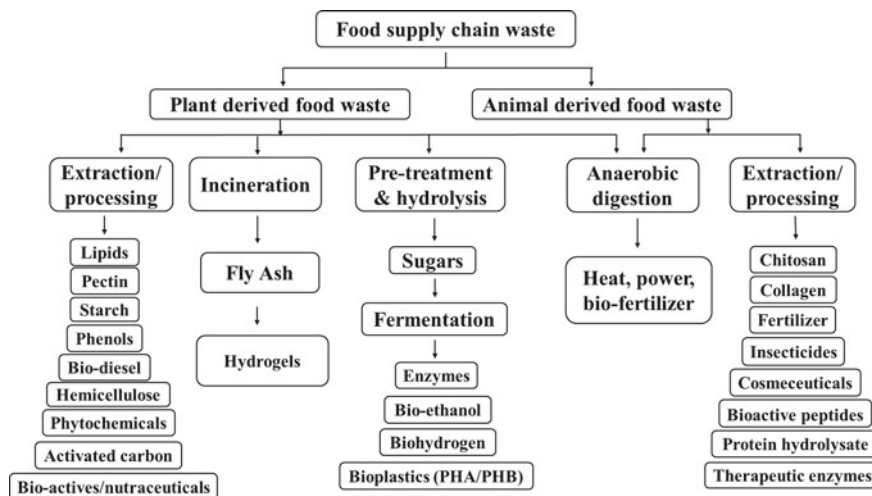


Fig. 1 Food supply chain waste can be converted into various commercial products

It is predicted that by 2023, demand for PLA will be doubled [32]. Recent research is focusing on the conversion of waste into high-value products like biochemical, biofuel, and biopolymers.

2 Waste as a Renewable Source

Food wastes are very good renewable resources as they can be transformed into various valuable products like biofuels and biochemicals. Biochemical compounds such as 2,3-butanediol [102] and succinic acid [128] are obtained from lignocellulosic substrates. These compounds can be used as precursors for biopolymers production. Under natural conditions, biopolymers are formed during complex cellular metabolic processes by enzyme-catalyzed polymerase chain reaction [101]. Natural biodegradable polymers are protein-based polymers (gelatin, albumin, and collagen) and polysaccharides-based polymers (chitosan, cellulose derivatives, and starch). Synthetic biodegradable polymers are poly-anhydrides, poly amino acids, acrylic polymers, aliphatic polyesters, poly-alkyl cyanoacrylates, and phosphorus-based polymers. The most abundant protein-based biopolymer is collagen derived from mammals. Polysaccharides can be derived from plants, animals, and microorganisms. Food industries can be divided into different categories based on the waste products such as grain processing industry (grain separator waste, husk, bran, fine dust, malt dust, straw, broken grains), fruit and vegetable processing industry (molasses, peel, distillate, vegetable washing water, pomace, beet pulp), meat, poultry, and seafood processing industry (shells of seafood, eggshells, skin, tendons, blood, and internal organs, contents of gastro industrial tract, bones), dairy processing industry

(hydrolysate and cheese residue, whey), and waste from brewery and distillery industries manufacturing coffee and tea (Spent coffee grounds, spent grains, carbonation sludge, bagasse, molasses). In Table 1, biopolymers produced from different industrial waste are summarized. Problem with wasted food is not only food loss but also

Table 1 Biopolymers produced from different industrial waste

Type of waste	Waste products	Food industries	Biopolymers	References
Waste from the grist mill, rice mill and malt house	Grain separator waste, husk, bran, fine dust, malt dust, straw, broken grains	Grain processing industry	PHA	[11, 19, 38, 72]
Waste from preparation and processing of fruit, oil mill, juice industries	Molasses, peel, distillate, vegetable washing water, pomace, beet pulp	Fruit and vegetable processing industry	Cellulose, lignin, PLA, pectin, xanthan gum, PHA (Carbon source)	[14, 28, 30, 36, 46, 62, 67, 122, 124]
Abattoir waste	Shells of seafood, eggshells, skin, tendons, blood and internal organs, contents of gastro industrial tract, bones	Meat, poultry and seafood processing industry	PHA, gelatin, Collagen, chitin/collagen	[10, 12, 15, 54, 74, 84, 88, 91, 92]
Waste from the milk production unit, cheese production	Hydrolysate and cheese residue, whey	Dairy processing industry	PHA (Nitrogen and carbon source), xanthan gum	[23, 78, 82]
Waste from the production of both non-alcoholic and alcoholic beverages	Spent coffee grounds, spent grains, carbonation sludge, bagasse, molasses	Waste from brewery and distillery industries manufacturers of coffee and tea	PHA	[24, 48, 80]

disposal issues [7]. So, some methods are approached to convert this food waste into valuable products such as fuels, chemicals, polymers, etc. Biorefinery term is used for conversion of biomass into various valuable products with the help of sustainable processing. This process has been used for many decades, but there is a need to develop such technologies which will produce novel products and cause less pollution. White biotechnology and green technologies are some of the most approached methods for the production of novel products [18, 26]. Potato is a very famous food all around the world, and while processing them a very large amount of waste emerges because of the quality failure, changes in color, and size.

Food waste from corn stover (leaves, husks, cobs, stalks, etc.) was used in biopolymers production. By degrading the lignocellulosic materials present in corn stover, polyols and PHA are produced. To synthesize biodegradable polyesters, these synthesized polyols could be utilized. Limonene can be extracted from citrus peels. Along with pectin, limonene can be used in biopolymer synthesis. Raw material for the industry of bio-based polymer coatings is derived from whey protein, soy protein, starch, PLA, and chitosan. Carbon and nitrogen are present in an ample amount in effluents from food and oil waste industries [96]. They can be used as raw materials for the production of PHA by fermentation. As demand for eco-friendly resources is increasing, market growth is favorable.

The waste from agro-industry such as the skin of potato; the skin of banana; the skin of citrus fruits; seed waste of grape, mango, pumpkin; the husk of peanut and wheat; coffee waste; bagasse and sugar molasses are rich in organic content like fatty acids, cellulose, starch, pectin, proteins, lignin, hemicellulose, sugar, etc. Agro-waste can be used as a renewable source for the production of biopolymer and can also be used as fertilizers, cattle feeds, and fuels.

Lignocellulosic material such as sugarcane bagasse is prolific in hemicellulose, cellulose, glucan, lignin, and xylan and can be used as raw materials for styrene-based biopolymers production. Carbohydrates and pectin are present in banana peels in high amounts and they can be used for biopolymer production [70]. Biopolymers such as PHA, PHB can be produced by using banana peel. In a study, chicken feathers and banana peels were used for biopolymer production. *Pichia kudriavzevii* VIT-NN02 is a yeast strain that was isolated from marine seaweeds. It is concluded that it can be used as a potential producer of bioplastic. The biopolymer from this study was identified as poly (3-hydroxybutyrate-co-3-hydroxyvalerate) [81]. As renewable sources, animal waste; marine waste; sea fish waste; carrot waste could be used for the production of the biopolymers. In biopolymers production at high levels, various strains of microorganisms were used. Different strains like *Thermus thermophiles* HB8, *Haloferaxmediterranei* DSM 1411, can be used in various biopolymer production like PHAs, (PHBV) poly-(3-hydroxybutyrate-co-3-hydroxyvalerate), 3-hydroxyvalerate from food waste like dairy whey. Various microbes like *Azobactercrococccum* and *Cupriavidussp.* KKU38 can be used in various biopolymer production like PHBs and PHAs from starch waste [114].

3 Biopolymers Production from Different Types of Waste

3.1 Biopolymers as Waste from Meat, Poultry and Seafood Processing Industry

Worldwide a large amount of seafood production is thrown away as processing waste such as shells of shrimps, oysters, krill, crabs, squid, fins, skins, viscera, and heads. They are very rich in polymer-like chitin/chitosan [2]. For the production of chitin, both chemical and biological methods were applied. In the process of the chemical method, the first step is deproteinization, followed by demineralization. In the process of biological methods, fermentation and enzymes are used for extraction. Green technology can be used to produce chitosan and chitin from agro-industrial waste by utilizing species like *Cunninghammellaelegans* and *Rhizopusarrhizus* [13, 33]. Applications of different biopolymers have been discussed in Fig. 2. Collagen is derived from mammals and is a protein-based biopolymer. Skin from pigs, their bones, skins from cattle, tendons, fish wastes (bones, scales), chicken processing waste, eggshells are used for collagen production. Discarded parts of fish, chicken, and egg are great sources for extracting collagen. Pepsin content, duration of hydrolysis, and acetic acid concentration are the factors on which collagen yield is dependent [8].

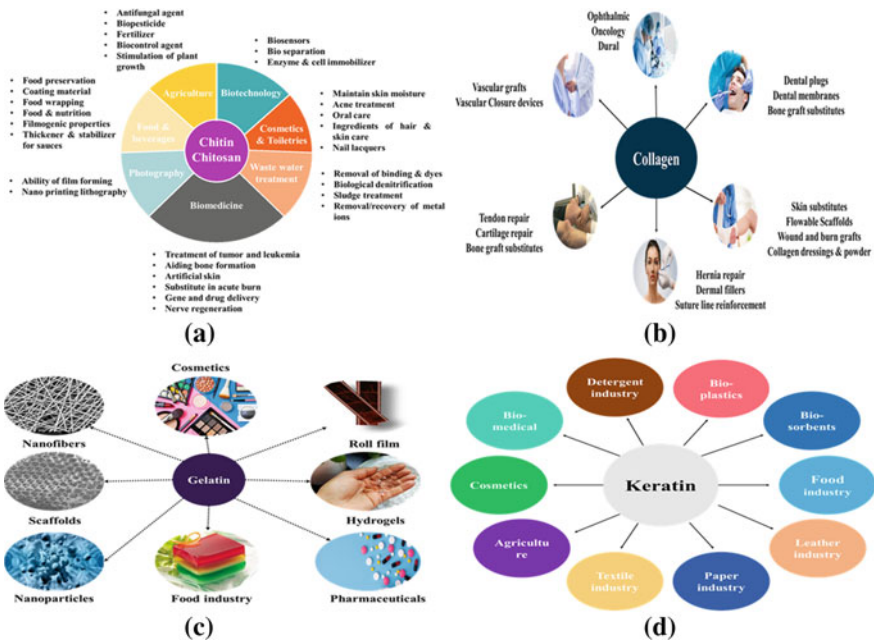


Fig. 2 Applications of various biopolymers

Table 2 Method of extraction and yield of collagen from different sources

Sources	Part	Methods	Time (hr)	Yield (%)	References
<i>Bramaaustralis</i>	Skin	ASC	48	01.5	[118]
Tilapia (<i>Oreochromis sp.</i>)	Scales	EHE	01	49.42	[44]
Sole fish (<i>Aseraggodesumbratilis</i>)	Skin	ASC	32	19.2	[9]
Giant croaker (<i>Nibea japonica</i>)	Skin	PSC	8.67	84.8	[132]
Yellowfin tuna (<i>Thunnusalbacares</i>)	Skin	ASC	24	3.18	[79]
Red snapper (<i>lutjanus sp.</i>)	Skin	ASC	48	9.7(Wet) 41(Dry)	[133]
Sea cucumber (<i>Acaudinaleucoprocta</i>)	Body wall	PSC	144	43.9	[63]
Cuttlefish (<i>Sepia pharaonis</i>)	Skin	ASC	–	01.66	[55]
		PSC	–	03.93	
Amur sturgeon (<i>Acipenserschrenckii</i>)	Cartilage	ASC	48	27.04	[61]
		PSC	48	55.92	

ASC = Acid soluble collagen; PSC = Pepsin soluble collagen; EHE = Extrusion-hydro-extraction

Collagen can be classified into salt soluble collagen (SSC), pepsin soluble collagen (PSC), acid soluble collagen (ASC), and ultrasound-assisted collagen (UAC) based on the extraction method used. Extracted collagen varied in the physiochemical properties and yield depending on the type of extraction method used. In Table 2, the method used for the extraction and yield of collagen is summarized.

Gelatin is a biopolymer mainly derived from bovines and porcine. It is majorly found in tendons, cartilage of animals, bones, and skin [120]. Gelatin is a widely used biopolymer in the photo industry (roll film, X-ray picture), Forensic, pharmaceutical (capsules, tablets, sugar-coated pills, vitamin encapsulation, styptic cotton), food industry (yogurt, soft sweets, beverage, jelly, packaging, films, coatings), Cosmetic industry (cosmetic, toothpaste, hair, and skincare products, lotions), and technical industry (match industry, paper manufacturing, adhesives, box making) [1, 4, 29, 37, 41, 95, 99, 100]. Wastes from the wool industry, slaughterhouses, and meat markets are the main sources of keratin [108]. Chicken feathers are considered one of the most important sources to extract keratin. Disposal of feathers to the landfills causes many environmental issues [94]. Hoof keratin shows promising results to be used in tissue engineering and biomedical fields [47]. Keratin has many industrial applications, it is used in cosmetics, pharmaceutical, biomedical, fertilizers, feedstock, environmental remediation, leather and textile processing, bioplastic films, coating, films, packaging, biodegradable composites, drug delivery, surgery and repairing, filter membrane and resins, bio-cement, Bio-ink [3, 35, 57, 71, 94, 109–113, 115, 126].

3.2 Biopolymers as Waste from the Agricultural Industry

Sugarcane bagasse is one of the main sources of lignocelluloses. Some other sources are corn cobs, banana, oil palm mesocarp, soybean straw, rice straw, wheat straw, soybean hull [124]. It is composed of ash, lignin (15–25%), hemicellulose (15–35%), and cellulose (35–50%) [87]. Ethanol solution and aqueous solution are used for the extraction of lignin. Enzymes such as manganese peroxidase and laccases can be used for enzymatic biodegradation of lignin. Before enzymatic hydrolysis, pretreatment of lignocellulosic matter is required for the production of biopolymer. These types of enzyme treatments help in yielding by-products like hydro cinnamic acid and vanillic acid. Lignocellulosic materials contain both cellulose and lignin and are considered a good source for the production of various biopolymers. Applications of lignocellulosic biomass are discussed in Fig. 3a. After cellulose, the most abundant plant material is hemicellulose. By alkali treatment, hemicellulose can be extracted from bagasse and cereal straw. Hemicellulose has many applications such as drug carrier, wheat gluten films, Wet-end additives in papermaking, new biomaterials, in the textile industry, in cosmetics, wound dressing, food additives, applicable as films, adhesives, gels, coatings [34, 43, 60, 64]. Cellulose-rich sources are peanut husk, rice, mango seed, citrus peels, wheat straw, fruit pomace. Cellulose content observed in apple, tomato, and cucumber are 8.81%, 8.60% and 16.13% respectively [122]. Rice husk was chemically treated with sodium hydroxide for extraction of cellulose and it is neutralized with HCl [116]. Cellulose has many applications in industries such as in pharmaceutical, cosmetic, food, biomedical, wood, bakery etc. [58, 65, 73, 105, 110, 123].

Food wastes like spent malt grains, citrus waste, cheese whey are the main sources of xanthan gum. *X. Campestris* is required for its production [68]. Jackfruit seed powder was combined with citric acid, peptone, KH_2PO_4 , and K_2HPO_4 for xanthan

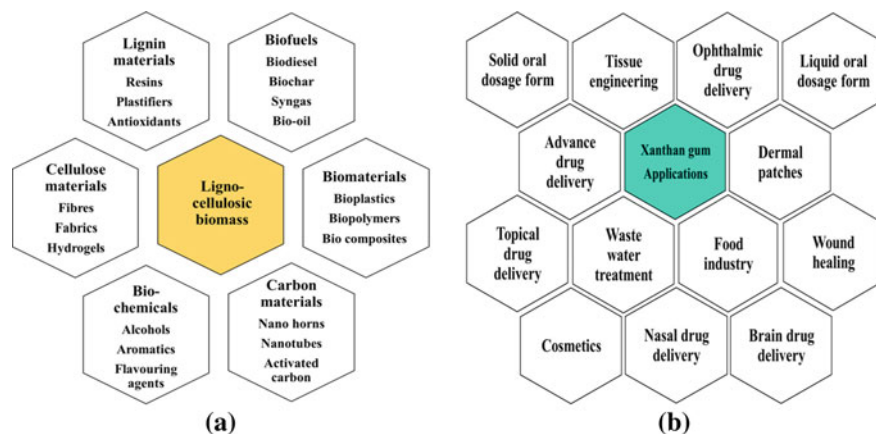


Fig. 3 Various applications of lignocellulosic biomass and Xanthan gum

Table 3 Concentration of xanthan gum from the different carbon sources

Substrate	Xanthan gum concentration (g/L)	References
Broomcorn stem	8.90	[121]
Shrimp shell	4.64	[27]
Raw starch-based media (cassava)	6.00	[51]
Kitchen waste	11.73	[59]
Date extract	11.2	[52]
Tapioca pulp	7.10	[40]

gum production by using *X. Campestris*. A yield of 51.62 g L⁻¹ was observed [49]. A study of xanthan gum production by bacteria *X. Campestris* from cocoa husks and coconut shells has also been done [25]. Table 3 shows the concentration of xanthan gum from different carbon sources. Figure 3b shows various applications of Xanthan gum [21, 31, 42, 75, 83, 86, 98].

3.3 Biopolymers as Waste from Milk, Agriculture, Beverage, and Meat Industry

Plastic has many applications in our daily life, since they are non-biodegradable, their usage leads to disposal issues [39]. There is much evidence that proves how the production of synthetic polymer causes harm to the environment [119]. Biopolymers are biodegradable, they can help in solving/reducing some environmental issues such as greenhouse gases and ocean pollution. PHAs are perfect substitutes for conventional polymers [50, 56]. Waste mass and agricultural residues are abundant, non-edible, and renewable carbon sources that are utilized in sustainable production for PHB. This process transforms waste into high-value products [50, 69, 93]. In comparison to their petrochemical counterparts, PHBs have very low environmental impacts [45].

Low biodegradability is one of the most critical issues of polymer-based industries. Biopolymers are replacing them as they are more eco-friendly and also biodegradable. PHA and PHB can be produced from various types of waste such as dairy waste, fish waste, bakery waste, sugarcane waste, potato waste, poultry waste, oil waste, fruit and vegetable waste, and rice mill waste. Biopolymers can be produced from dairy waste by microbial production. Dairy waste is rich in fats, grease, phosphates, oils, minerals, suspended solids, and soluble organics. From dairy waste, the most synthesized biopolymer is PHB [17, 104]. Biopolymers produced by microbial strains using dairy waste are summarized in Table 4.

Wheat straw is used as a substrate for PHB production by *Burkholderia sacchari* DSM17165 [20]. *Burkholderia sacchari* DSM17165 is used for the production of PHB, while wheat straw is used as substrate [21]. For the production of PHA, the

Table 4 Biopolymers produced by microbial strains using dairy waste

Source	Microbial strains	Biopolymers	Yield	References
Whey	<i>Ralstoniaeutropha</i>	PHB	0.17 g L ⁻¹	[66]
Whey and corn steep liquor	Recombinant <i>E. coli</i>	PHB	6.12 g L ⁻¹	[77]
Milk whey	<i>X. campestris</i> sv. <i>campestris</i> -2149	Xanthan gum	21.91 g L ⁻¹	[76]
Cheese whey	<i>Xanthomonascampestris</i> sp. <i>Mangiferaeindicae</i> IBSF 1230	Xanthan gum	46.8 g L ⁻¹ of gum	[68]
Whey	Dairy wastewater as inoculum	PHA	0.284 g L ⁻¹	[17]
Cheese whey lactose	<i>Xanthomonascampestris</i> and <i>Xanthomonaspelargonii</i>	Xanthan gum	0.42 g of xanthan g ⁻¹ of lactose; 0.27 g of xanthan g ⁻¹ of lactose	[78]
Fermented cheese whey	Activated sludge	PHA	28.2 g L ⁻¹	[23]
Cheese whey	<i>Haloferaxmediterranei</i>	P(3HB-co-3HV)	9.6 g L ⁻¹	[82]
Whey supernatant	<i>Thermusthermophilus</i> HB8	PHA	0.57 g L ⁻¹	[85]
Whey Permeate	<i>Pseudomonas hydrogenvora</i>	PHA	21.91 g L ⁻¹	[76]
Whey lactose	<i>Haloferaxmediterranei</i> <i>Pseudomonas hydrogenvora</i> <i>Hydrogenophagapseudoflava</i>	PHA	5.5 g L ⁻¹ 1.3 g L ⁻¹ 2.7 g L ⁻¹	[53]
Lactose and whey permeate	<i>Sinorhizobium</i> 41 <i>meliloti</i> , <i>Hydrogenophagapseudoflava</i> DSM 1034	PHA	<i>Sinorhizobium</i> 41 <i>meliloti</i> : 0.483 g L ⁻¹ <i>Hydrogenophagapseudoflava</i> : 0.375 g L ⁻¹	[90]

Table 5 Agro-industrial waste is used as a carbon source for the production of biopolymers by using microorganisms

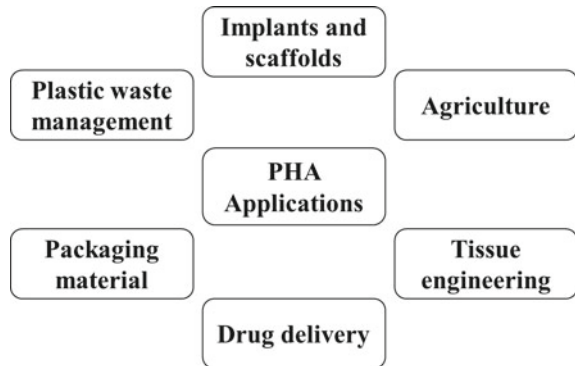
Residue	Producing microorganism	Biopolymer	Yield	References
Cane juice	<i>L. confusus</i>	Exopolysaccharides	62 g/L	[106]
Jatropha	<i>Pseudomonas oleovorans</i> ATCC 29,347	PHA	26.06 g/g	[5]
Wheat cob	<i>Burkholderiasacchari</i> DSM 17,165	PHB	0.22 g/g	[20]
Used palm oil	<i>Cupriavidusnecator</i>	PHB	0.8 g/g	[97]
Rice straw	<i>B. sphaericus</i> 0838	PHB	0.08 g/L	[117]
Rice Straw	<i>B. cereus</i> PS 10	PHB	10.61 g/L	[107]
Corn cob	<i>Inonotusobliquus</i> (CBS314.39)	Exopolysaccharide	Not quantified	[130]
Coconut water	<i>Lactobacillus confuses</i>	Exopolysaccharides	18 g/L	[106]
Tequila bagasse	<i>Saccharophagusdegradans</i> ATCC 43,961	PHA	1.5 g/L	[6]
Frying oil	<i>C. necator</i> H16 NCIMB10442	PHB	1.2 g/L	[129]
Chicken feathers	<i>Morchellaesculenta</i>	Exopolysaccharide	4.8 g/L	[125]
Rice straw	<i>B. firmuss</i> NII 0830	PHB	0.16 g/L	[117]
Jute	<i>Bacillus megaterium</i> RB-05	Exopolysaccharide	0.297 g/g	[22]

main sources are wheat, plant saps, rice bran, molasses [11]. Various microorganisms are used for the production of biopolymers from agro-industrial waste (Table 5).

Vegetable waste like carrot, fennel, and tomato can produce PHB [28]. This waste carbon source is used by strains like *Bacillus thermantarcticus*, *Halobacillusalkaliphilus* (type strain FP5; DSM18525), *Haloterrigena hispanica* (type strain FP1; DSM18328) for the production of PHB. By using *Halomonas* i4786, fruit processing water and leguminous processing water can be used as a substrate for the production of PHA.

Fermented shrimp paste is used to isolate *Salini vibrio* sp. M318 bacteria. For biopolymers synthesis, some sources such as potato waste, citrus peels, coconut waste, animal fats, mango seed, peanut seeds, and waste cooking oil can be used. Oils such as tallows and waste oils can be used as a carbon source in the fermentation media. As these oils do not require any pretreatment. Oils can be easily collected from industrial and household waste. In a study, a noxious weed water hyacinth biomass (WH) is converted into PHB by *Ralstonia eutropha*. For hydrolysis of WH, alkaline

Fig. 4 Applications of PHA in various fields



pretreatment was performed. To properly understand the optimization conditions, further study is required. This study shows that WH biomass can be used for the production of bioplastics [103].

Various applications of PHA are shown in Fig. 4. PHB has many applications in various fields such as biomedical (Sutures, dressings, surgical implants, engineering of heart valves and pins), Packaging (food packaging), agricultural (encapsulation of fertilizers), environmental (bottles, bags, films of involvement, disposable items, personal hygiene items), Pharmacological (encapsulation of medicines for controlled release), etc.

4 Challenges

Regarding biodegradable biopolymers, researchers have different different opinions on the acceptability of biopolymers. Although biopolymers have many advantages, they also have some disadvantages like high hydrophilic capacity, low mechanical properties, and rapid degeneration rate. Their applications do not work feasibly in humid conditions. Biopolymers can replace synthetic polymers but due to some limitations, it is difficult to adapt them rapidly. To modify the properties of biopolymers, many techniques are being studied. In the future, it is possible to replace synthetic products with biopolymers.

5 Conclusion

An enormous amount of waste generated from different industries and disposed of at landfill sites is becoming an environmental concern. Waste is considered a renewable source for many high-value products such as biofuels, biochemicals, biopolymers, enzymes, etc. Researchers are focused on the production of biopolymers from

various waste as it has wide applications in the pharmaceutical industry, food industry, cosmetics, leather industry, biomedical, drug delivery, agriculture, textile industry, paper industry, in nanoparticles, in waste management. Using a sustainable, innovative, and environment-friendly approach, these wastes can be transformed into biopolymers. Future studies should focus on improving the properties of biopolymers, increasing their scalability to industrial scales and pilot plants. Green technologies should be explored more for the extraction and production of biopolymers. This would help in the management of waste and aid in environmental problems.

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Biopolymers and Environment



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Abstract Biological polymers are versatile class of chemicals that are either synthesized from biological resource or fabricated by biological systems. Novel biopolymers are classified based on their origin, which includes natural and synthetic biopolymers. Currently, biocompatible and non-toxic biopolymers have been used to develop efficient systems for the applications in different fields. Especially, in recent times, such materials have gained more attention in biomedical field (tissue engineering, wound healing, burn dressing, and fungal infection). These

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19

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biopolymer composites are efficient in protecting and discharging bioactive drugs including nutraceuticals, pharmaceuticals, enzymes, and probiotics. Hence, this chapter provides an overview of the importance of bio-based polymers, fabricated or degraded naturally, classification, applications and biological activities.

Keywords Biopolymers · Classification · Genetic engineering · Biological activities

1 Introduction

Biological polymers are a class of “giant” fragments that contain different structural components connected together to generate extended chains. Among them, simple constituents are named monomers, on the other hand, more-dense constituents linked together are referred to as complex polymer. If the polymer has same component repeatedly this is referred to as repeated unit. Generally, biological polymers are defined as “a polymeric chain generated under natural environments during the growth cycles of living organisms”. Hence, they are named natural polymers. Novel biopolymer materials are fabricated naturally from plants, animals, bacteria, and fungi. Biopolymer-based materials have been investigated widely for delivery applications due to their biocompatibility, biodegradability, energy efficiency, inexpensive, non-toxic in nature over the synthetic ones [4, 6, 17, 59, 62, 65, 84]. For instance, Agar–agar and alginates are extracted from red and brown algae, which cultivate abundantly in the normal environment [54]. In recent times, drug delivery system gained more attention in pharmacokinetics. Biopolymers are actively used or enhanced in drug carrier systems and thereby they can be utilized in ocular, transdermal, dental, or intranasal delivery systems in living organisms [29]. These are generated inside the cells by multifarious metabolism. For example, applications of nanomaterials, carbohydrates like cellulose and starch components are used mostly due to their prominent ability. Recently, it was observed that along with these materials, there was growing attention in more multifarious hydrocarbon polymers synthesized in organisms including bacteria and fungi, particularly polysaccharides like xanthan, curdlan, pullulan, chitin, chitosan, and hyaluronic acid [63]. New generations of biomaterials are developing day by day in various areas of research field and received more consideration as for the possible replacement of existing products like conventional plastics [55].

In the present scenario, there has been a lot of priority given more towards good quality of environment due to the existence of contaminants, produced by chemically synthesized materials. Hence, researchers were started for development of new class of materials by combined process of green chemistry and engineering technology [33, 59, 66, 84]. For example, in recent time, each country is understanding the exhaustion of resources of petroleum products, hence, looking for an environmentally friendly material that can be manufactured without being dependent on petroleum products. It has been observed that there is an enormous amount of utilization of polymers

compared to other materials, because polymers have been found more applications in all kinds of fields [17, 33, 62, 66]. But, chemically synthesized polymeric materials found an impact on living organisms. Hence, there are growing demands on the development of biodegradable polymeric materials which must be an environmental friendly and can be prepared by biological molecules like lipids, polysaccharides, and proteins [55]. Here, in this chapter, we are discussing an overview of the importance of bio-based polymers.

2 Classification of Biopolymers

Though it was observed that different elements are involved in synthesis of synthetic organic polymers, major elements are found to be carbon (C), hydrogen (H), oxygen (O), and nitrogen (N). Biopolymers on basis of synthesis may be classified as

- i. Natural biopolymers
- ii. Synthetic biopolymers

2.1 *Natural Biopolymers*

Natural polymers can be produced directly from the microorganisms [60], plants, and animals. These Monomeric units of biopolymers like chitosan, alginate, collagen, gelatin, cellulose, hyaluronate, silk, fibrinogen, and starch exhibit immense potential in the medical domain [6, 10]. Natural biopolymer offers certain advantages of being biodegradable and biocompatible. Biodegradation process occurs through the chemical deterioration and the action of enzymes correlated with living organisms [79]. Recent studies reported that natural biopolymer-based electrical sensing devices are utilized in a series of distinctive biopolymer hydrogels including silks, gelatin, cellulose, sodium alginate, chitin, and chitosan, etc. [15]. On the other hand, isolated natural biopolymers from different sources of environment for instance polysaccharides derived mainly from seaweeds, chitosan from insects as well as crustacean's shells of certain other organisms [1]. Isolated biopolymers from living organisms are renewable, non-toxic, and environmentally benign.

Nowadays, naturally obtained polymers are considered as smart materials because they offer flexible and tunable podium to make the suitable condition for development of a utilitarian extracellular matrix which competent to help regenerating the target tissue, while contrasting the onset of adverse events [70]. *Gum Arabica* is one of the well-known natural gum plant which has gigantic applications in producing ionic devices including batteries, sensors, bio-sensors, and other electronic applications.

2.2 Synthetic Biopolymers

Synthetic biopolymers are human-made polymers that can artificially synthesize/create in a research laboratory [67]. Synthetic biopolymers are resources synthesized by artificial chemistry from diverse biological sources including vegetable oils, sugars, fats, resins, proteins, amino acids, etc., have been considered as well-known biopolymers [25]. Further, synthetic biopolymers are created by polymerization processes from natural plant and animal fibers with low molecular weight which make up a large category of polymers, for example, nylon, polystyrene, polyvinyl chloride, and polyethylene. These are commercially produced polymers which we used routinely in our daily life polyethylene produced from plastic and nylon fibers typically used in preparation of clothes, fishing nets, etc. On the other hand, synthetic polymers are usually derived from petroleum oil in the proscribed environment [67]. The organic nature of synthetic polymers is made up of carbon-carbon (C-C) bond as their backbone [82].

3 Role of Plant-Derived Biopolymers in Agriculture

Bio-based polymers are used in various applied domains such as medicine, packaging, agriculture, and other areas of research because they have ability to degrade short life-span as compared to petroleum-based polymers [26]. Various biopolymers can be produced in major quantities from lower and higher plants. The biopolymer chitosan (CHT) is a deacetylated chitin, synthesized from fungal cell wall and exoskeletons of arthropoda. Rahman et al. [53] study revealed that chitosan biopolymer significantly enhanced the growth, yield, and biochemical constituents of strawberry fruits higher than 42% compared to untreated fruits. Moreover, CHT also induces plant growth by enhancing physiological process such as cell elongation, cell division, enzymatic stimulation, and production of proteins that could ultimately lead to increased yield [13]. Naturally occurring chitin and chitosan have potential to control plant diseases against different pathogens of various crops. Agriculture raw materials like cereals and grains (like maize, sorghum, and rice) are extremely rich in biopolymers including starch, proteins, nucleic acids, lipids, and polysaccharides. Furthermore, liner polyester easily degrades bacteria in agriculture wastes which have applications in agricultural film [47]. According to [44], microorganisms play a significant role in the fabrication of varied biopolymers, for instance, polysaccharides, polyesters, and polyamides. Agricultural oil can be synthesized from these inexpensive carbon sources which were used to produce different kinds of biopolymers [49]. Polymeric biocides exhibit many significant beneficial applications in agricultural field such as reduction of toxicity, eliminate time and cost, less active materials needed, reduce widespread distribution, and protect them from environmental degradation. Moreover, polymer herbicides carry major drawback for their economic use and disposal of herbicide residue which could be negative impact on

soil and plants. Hence, researchers made some attempts to decrease this problem from farming deposits having polysaccharides, for example, bark, sawdust, cellulose, and other cellulosic wastes [19]. Therefore, the use of extreme quantity of such bioactive polymers typically obligatory for herb control is inevitable [19].

The review studies explore on using some plants such as grape pomace, tomato pomace, pineapple, orange, lemon peels, sugarcane bagasse, rice husks, wheat straw, corn starch, and palm oil fibers, are excellent products derived from agricultural wastes to obtain biopolymers [56]. According to recent report of Food and Agriculture Organization (FAO), it has been estimated that between 20 and 30% of fruits and vegetables were thrown out in farms as waste material in post-harvest handling [39]. However, increase in the production of plastic waste originates in agriculture field from solar shading nets, organic mulching materials, and pesticide receptacles. Green-based polymers absorb ethylene, maintain temperature, eliminate water vapor, and so on [85]. Moreover, biopolymer-based hydrogels contain various active compounds which are widely utilized in various fields of research like farming, mostly as water retention agents for soil and carry agrochemicals for their sluggish or sustained-release [73]. Agricultural residues produced from different parts of the plants such as almond shells, walnut shells, pruning fibers of orange tree, husk-fiber of rice, bamboo, jute, flax, and among others as complex resources could be useful for diverse industrial applications [75]. Biopolymer-based biostimulants endorsed most intense root growth and also elucidate morphological, physiological, and metabolomics changes that occur in fruiting vegetables like tomato, eggplant, pepper, melon, and watermelon [37]. Hence, biopolymers play a significant role in the making of novel plants which delivers an actually bio-renewable way for their production.

4 Genetically Engineered Biopolymers

Genetically engineered (GE) protein-based biopolymers have some defined monomer compositions, molecular weights, sequences, and stereochemistry [40, 41, 43]. Genetically engineered elastin-based biomaterials are biologically inspired in biomedical applications like cell culture, tissue engineering, protein purification, surface engineering, and controlled drug delivery [58]. Genetically modified plants can have many potential applications in different fields of biomedical research such as antigens, therapeutic agents, monoclonal antibody fragments biopolymers, and so forth [77]. Genetically engineered biopolymers synthesis has been shown in Fig. 1.

Polymers containing sequence of peptide molecules having repeats in which individual repeating unit can be formed two to several hundreds of amino acid constitutes, and may persist from a little to more than 100 times [74]. Here, poly-amino acids are found to be either homo and/or copolymers formed by chemical polymerization of a lone amino acid or a combination of amino acids, respectively [24]. Natural biopolymers are difficult to obtain from natural sources; however, this is only achieved by using tools of genetic engineering, for instance, protein-engineered biopolymers

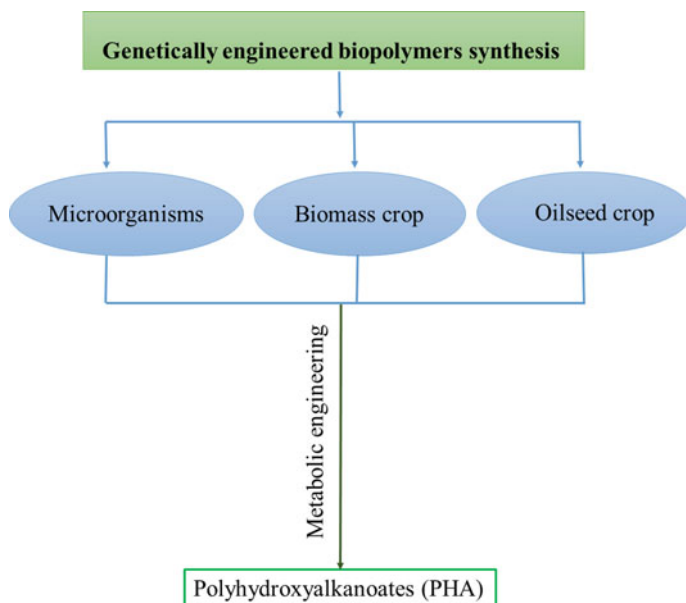


Fig. 1 Schematic representation of synthesis of biopolymers by different sources

made up of completely recombinant proteins in which amino acid sequence act as monomers of that biomaterials [57]. The desired protein sequence of amino acids is encoded into a deoxyribonucleic acid (DNA) using recombinant DNA (rDNA) technology. Novel biopolymers synthesized and characterized using recombinant DNA (rDNA) process will be studied, and the significant benefits of this procedure were used for the design of novel polymeric drug delivery systems [46]. Genetically engineered protein-based polymers have received attention due to their tremendous applications in material science and engineering. Recent studies reported that the recombinant technology has fixed to take control on genetic sequence and protein properties of given elastomeric protein biopolymers [72]. These features of recombinant protein technology are useful in the preparation of various functional materials for regenerative medicine.

On the other hand, biopolymers are constructed from DNA and RNA nucleotides. RNA is found to be more flexible when compared to DNA, because RNA is structurally more versatile and can be original molecule of life [68]. The identified biopolymers exhibit some facial appearance as they have ability of self-replication, carry entirely the genetic data stand-in as the blueprints for proteins, and catalyze chemical reactions. Additionally, biopolymers play a significant role in gene delivery including DNA plasmids, RNA, and siRNA delivering at target site [51]. The study of [34] suggested that recombinant technology provides entrenched protocols including mutation, gene fusion and cloning for the appearance of peptides and proteins. An experimental study reported that genetically modified plants like tobacco and

Arabidopsis thaliana are being investigated as transgenic host for silk proteins, yield of these plants enhanced up to 2% of tobacco leaves and 8.5% of *A. thaliana* leaf apoplasts [76]. According to [18], the transgenic plants include *Camelina sativa*, *Nicotiana tabacum*, and *Saccharum officinarum* as a good source of polyhydroxyalkanoates (PHAs), and maximum level of (PHAs) accretion in plants was attained in transgenic *A. thaliana*. Plant genetic engineering could improve biomass characteristics by developing crop varieties that self-produce cellulase and/or ligninase enzyme for cellulose degradation as well as lignin degradation [69]. Hence, plant genetic engineering could increase in biomass production using transgenesis in model as well as in crop plants under different environmental conditions. Therefore, genetic modified plants can be potentially better biomass source for biopolymer production.

5 Impact of Biopolymers on the Environment

Since the last decades, biopolymers received much attention in the area of research because of their unique characteristics. Biopolymers are biodegradable, non-toxic to the other organisms including human, and eco-friendly for agriculture [50]. Biodegradable polymers are isolated from natural atmosphere, with atmospheric CO₂ being fixed into biomass and that could be converted into polymer. In fact, these biopolymers degrade anaerobically in a landfill emits CO₂ and CH₄ [12]. Biodegradation process takes place in various ecological conditions like soil, compost, marine, and other aquatic systems. Biodiversity of microorganisms occurs on terrestrial ecosystems, which allow the biological breakdown to be more achievable with respect to other surroundings, like water or air [45].

Compostable polymers undergo degradation process occur in which carbon-based matter is transformed into CO₂ and humus by the activity of a diverse collection of microorganisms. Microbial systems have received much attention due to their greater participation in fabrication of biopolymers using *Leuconostoc mesenteroides*, *Pseudomonas pseudomallei*, and *Bacillus* spp. [47]. Synthetic compounds are non-biodegradable; they pose serious threat to the environment and create many ecological problems. Environmental pollution may increase due to the manufacturing and incineration of plastics which occur in both terrestrial and aquatic ecosystems.

6 Biological Activities of Biopolymers

Novel biopolymer materials fabricated naturally used numerous biological activities (Fig. 2) like antioxidant, antimicrobial, anticancer, anti-inflammatory, neuroprotective, and immunomodulatory activities (Table 1).

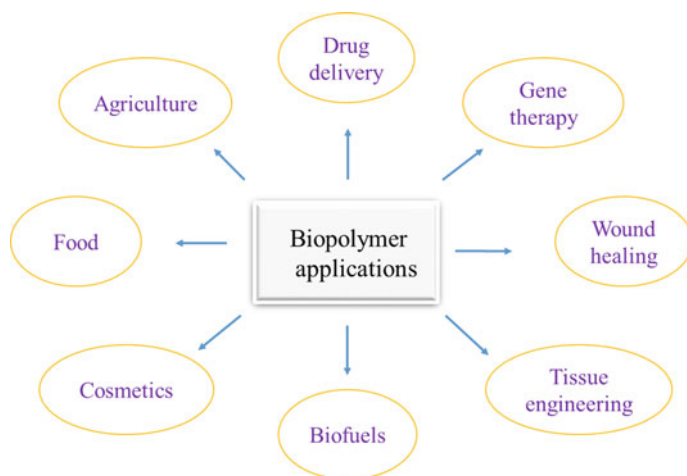


Fig. 2 Schematic representation of applications of biopolymers

6.1 Anticancer Activity

Cancer is one of the most dangerous infectious diseases which are affecting extreme mortality in humans; researchers are in the search of plant-based medicine as a safe and different medicine. Pharmacologically active biopolymers are isolated from root extracts of *Symphytum asperum*, and *Anchusa italica* utilizes anti-cancer efficacy against human prostate cancer via targeting androgen receptor, cell cycle arrest, and apoptosis [7]. Recent literature revealed that Curcumin is metabolite extracted from the plant *Curcuma longa*, inhibits the proliferation and invasion of tumors by the suppression of signaling pathways and its effectiveness against breast, lung and prostate cancer has been well documented [36]. Gene therapy is another innovative way to treat various types of cancer which involves small interfering RNA molecules (siRNA); these siRNAs decrease the regulation of the BCR-ABL region of chronic myeloid leukemia (CML) [5, 38]. Flores-Cortez and his group study revealed that anti-tumor activity of peptides derived from marine *Vibrio* sp. extracted biopolymers induced breast cancer in rats (Flores-[21]).

6.2 Antioxidant Activity

Free radicals are molecular species synthesized by cellular metabolism as intermediates and comprise unpaired of electron in an atomic orbital. These molecules can act as oxidants and/or reductants by accepting an electron or donating electron to other molecules [81]. Reactive oxygen species (ROS) is common product of aerobic cellular metabolism, increase ROS level may cause oxidative stress, hence

Table 1 Biological activity of biopolymers isolated from different plant materials

Biological activity	Plants	Common name	Compounds responsible for biological activity	References
Antibacterial activity	<i>Acacia Arabica</i> (Lam.) wild	Babul	Cyanogenic glycosides	[9]
	<i>Neolamarckia cadamba</i>	Burflower-tree	Tannic acid	[30]
Antifungal activity	<i>Capsicum baccatum</i> L	Locoto	α -amylase	[78]
Anticancer activity	<i>Camptotheca acuminata</i>	Happy tree	Pentacyclic group of quinoline alkaloids;	[35]
	<i>Scoparia dulcis</i> L	Sweet-broomwort	Polyoxygenated flavone	[52]
Antioxidant activity	<i>Adenantha pavonina</i> L	Red wood	Galactomannan	[42]
Immunomodulatory activity	<i>Terminalia Arjuna</i>	Arjuna tree	Arjunic acids like 2,3-di-O-acetyl arjunic acid, 2,3-di-O-benzoyl arjunic acid and 2-O-p-anisoyl arjunic acid	[61]
Neuroprotective activity	<i>Momordica charantia</i> L	Bitter gourd	Phytosterols, terpenoids, fatty acids, phenolic compounds, phenolic acids, and flavonoids	[16]

damage to tissues. The excessive generation of ROS leads to oxidative stress and thereby causing disintegration of DNA, lipid peroxidation, and protein oxidation. ROS and antioxidant defenses maintain balance in the living organisms systematically including glutathione, superoxide dismutase (SOD), catalase (CAT), and peroxiredoxins (PRXs) which play key role in the cellular signal transduction and keep oxygen homeostasis in the biological environment [14]. Antioxidant properties of biopolymer/candelilla improved homogeneity of wax in the protein films when compared to compare to water-swollen films [32]. Catechins are natural polyphenolic compounds that are widely utilized as nutraceuticals for improving antioxidant [28]. Biopolymer-mediated nanocomposites may be considered as noble formulations (i.e., F₃ and F₆) to recover bio-accessibility and antioxidant ability from kenaf seed flour reported by [3]. In another study, results revealed that the biopolymer isolated by *A. pavonina* seeds showed higher antioxidant activity and more potent than polysaccharides obtained from *Schisandra sphenanthera* [42]. These studies proved that biopolymers have potential source of antioxidant activity.

6.3 Antimicrobial Activity

Biopolymer derived compounds can be used against various types of microbes, including bacteria, fungi and virus which could infect plant, animal and human. Various studies exhibit potential antibacterial, antifungal, and antiviral activity. Biopolymer isolated from a bacterium *Klebsiella terrigena* improved inhibitive capability against all the selected gram-positive and gram-negative pathogens [31]. Modified biopolymers exhibit superior antimicrobial activities which enhance the cell membrane permeability of *S. aureus*, *S. pyogenes*, and *E. coli* cells [64]. The major mechanism of antimicrobial activity of chitosan against *Streptococcus iniae* which inhibit the bacterial cell growth and thereby breaking the cell wall which will lead to leakage of cytosolic contents and ultimately leads to cell death or necrosis [8]. In a study, [71] displayed that Starch-based biopolymers and biocomposites obtained from lemon grass and cinnamon essential oils are responsible for antimicrobial activities against bacteria (*E. coli*, *S. aureus* and *A. niger*) and fungi (*C. albicans*, *P. commune* and *E. amstelodami*), respectively. Molecular mechanisms of bacterial polymer including polysaccharides, polyamides, polyesters, polyphosphates, extracellular DNA, and proteinaceous components play significant role in pathogenesis [20].

6.4 Anti-inflammatory Activity

Biopolymers are being used clinically as inflammation. It protects body from harmful stimuli and begins the healing process. Naturally obtained versatile biopolymers have an admirable anti-inflammatory activity in-vivo, so that it can be employed in biomedical domains for chronic wound management [11]. The multifunctional biomaterials not only promote the regeneration but also combat infectious disease and modulate inflammation [22]. The improvement of biopolymer-based ROS scavengers and/or united with different drug molecules has become a promising approach for the treatment of acute and chronic human inflammatory diseases [83]. Potential applications of biopolymers used to treat various human diseases by inflammation including atherosclerosis, heart disease, stroke, cancer, diabetes, bone arthritis, asthma, and others.

6.5 Neuroprotective Activity

Neuronal cells are highly susceptible and have certain mechanisms and strategies which are used to defend against from neuronal injury, dysfunction, degeneration, and apoptosis in the central nervous system (CNS) are recognized as neuroprotection [48]. The mechanism of action demonstrated that biopolymers have an inhibitory effect on

caspsase(s) enzyme activity and affecting the mitochondrial transmembrane potential. Curcumin is a polyphenol synthesized from the rhizomes of turmeric. Biological effects were studied using in-vitro axotomy model of key hippocampal neurons. CurcuEmulsomes validate significantly the potential to succeed neuroprotection against neuronal injuries in the CNS [80].

6.6 Immunomodulatory Activity

Since from the last few 10 years, various novel biopolymers have been extracted from medicinal plants and utilized as a source of therapeutic agents. Recent study suggested that the biopolymeric fraction RLJ-NE-205 isolated from the rhizomes of *Picrorhiza kurroa* stimulated both the humoral and cellular arms of the immune system [23]. Protein-based biopolymers isolated from *Salicornia herbacea* may initiate immune response primarily by activation of macrophages but also can serve as effector cells [27]. Potential of exopolysaccharide (EPS) produced by wild type and mutant *Weissella confuse* strains to enhance host immunomodulatory functions via activation of macrophages and lymphocytes [2].

7 Conclusion

Plant-based biopolymers are gaining lot of attentions and were continuously using in different fields of science and technology. These naturally derived polymeric substances are generally isolating from natural resources and then they are used as raw compounds for biomaterial preparation. They generally offer biocompatible, biodegradability, non-toxic and energy efficiency than the synthetic ones. Synthetic polymers have been using high radiation and toxic chemicals that are harmful to the environment and to human health. Moreover, material-based natural biopolymers include proteins, and polysaccharides have been found as biocompatible and non-toxic for the human body. Here, we overviewed on biopolymer properties especially biological activities (i.e., enhances the cell proliferation and tissue regeneration) which are used for in the treatment of life threatened diseases.

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Biopolymers: Global Carbon Footprint and Climate Change



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Abstract Greenhouse gas emissions particularly carbon dioxide emissions are increasing with the intensifying of worldwide conventional plastics requirements. The ecological and environmental problems associated with fossil-based plastics (carbon dioxide emissions and fossil-based waste) and safeguarding of natural resources result in the transition from non-biodegradable petroleum-based polymers to greener biodegradable polymers. Polyhydroxyalkanoates and polylactic acid are favorable alternatives, which can replace petroleum-based polymers in numerous industrial fields (agroindustry, food/beverage packing, medical, pharmaceutical, and hygiene). This chapter offers an overview of the polyhydroxyalkanoates and polylactic acid biodegradability under various environments. Finally, some aspects related to the carbon footprint and climate change have been provided.

Keywords Carbon Footprint · Climate change · Greener biodegradable polymers · Microbial degradation packaging · Polyhydroxyalkanoates · Polylactic acid

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1 Introduction

The first twenty years of the twenty-first century have been marked by a significant rise in the global economy [1]. However, the *economic progress has been* accompanied by an exacerbated environmental concern because of the global greenhouse gas emissions (GHGs) related to fossil-based polymers production [2–5]. The sharp rise in the requirement for petroleum-based polymers is increasing, by the year 2050, their production being expected to have tripled. This results in enormous negative effect on the biosphere, especially on the GHGs and climate change [2, 5–12]. The fossil-based polymers are looked at as a growing source of waste; billion metric tons of plastics appear in landfills, out of that, a small part is recycled (around 9%), and the other small part is incinerated (around 12%) [10, 11, 13–16]. From an environmental perspective, mechanical recycle represents usually the best alternative, but it's not the most economically favorable option (substantial costs, huge energy consumption, and more GHGs) [10, 17, 18]. Moreover, the recycle can lead to downcycling products of lower quality; much of the polymer-based materials can solely be recycled a few times, then they appear in landfills or can be incinerated. The plastics incineration has a severe environmental impact through CO₂, a primary driver of worldwide warming and climate change [10, 15, 19, 20]. Most fossil-based polymers end up in landfills, accumulating in the natural environment especially in the ocean and causing damage to the ecosystem [15]. In this context, the minimization of problems associated with fossil-based plastics results in the transition from non-biodegradable polymer-based materials to bio-based biodegradable materials as a very attractive alternative, owing to their eco-friendly features (renewability, recyclability, biodegradability, lower GHGs, and lower energy consumption than fossil-based polymers) [8, 10, 21–28]. Bio-based polymers represent a significant part of the bio-economy, and in 2020, the total of their production volume reached 4.2 million tons, corresponding to 1% of the fabrication capacity of petroleum-based polymer materials [29]. These are attracting the interest of a variety of industrial areas (agroindustry, biocatalysis, medical, pharmaceutical, food/beverage packaging, hygiene products, and automotive) [30–42]. Biopolymers are bio-based polymers produced by algae, plants, animals, and bacteria that show biodegradability and sequestration of atmospheric carbon as their undeniable advantages [1, 24, 43–45]. Biodegradability is the potentiality of the biopolymers to be completely disintegrated by heterotrophic microorganisms, while biodegradation is a process by which biopolymers are completely disintegrated by several microorganisms into natural substances and biomass [13, 14, 28–31, 46–54]. More specifically, synthetic biopolymers such as polyhydroxyalkanoates (PHAs) and polylactic acid (PLA) have emerged as a promising, renewable, and biodegradable alternative, being the largest contributors to the development of bio-based packaging materials, and a sustainable circular economy [10, 25, 29, 55, 56] (Fig. 1).

PHAs and PLA can undergo mineralization in landfills, soil, fresh water, ocean, and industrial composting facilities, depending on the numerous essential factors (biopolymer material, environmental and microbial factors) [4, 10, 13, 14, 16, 48, 51,

Fig. 1 Promising characteristics of polyhydroxyalkanoates and polylactic acid, which contribute to a circular/resilient economy



57–62]. This title offers an outline of the polyhydroxyalkanoates and polylactic acid biodegradability under different environments and points out some aspects related to the carbon footprint and climate change.

2 Biopolymers and Biodegradation

Biopolymers are polymeric biomolecules based on monomeric components, mainly covalently joined. The prefix *bio* means that the biopolymers are bio-based carbon materials, fully or partially extracted from natural biomass (algae, plants, animals, and microorganisms), while polymers are fossil-based carbon materials [1, 24, 29, 44, 45, 62–72]. Biopolymers (green polymers) can be classified according to their source into renewable natural-based biopolymers (polyssacharides-based and protein-based) and renewable synthesized biopolymers from biomass (directly synthesized from biomass by microorganisms such as polyhydroxyalkanoates PHAs and indirectly chemically synthesized biopolymers such as polylactic acid PLA) [10, 25, 48, 73]. The synthesized biopolymers from biomass can be either biodegradable (PHAs and PLA) or non-biodegradable (bio-polyethylene, bio-polyethylene terephthalate, bio-polypropylene, and polyol-polyurethane, these being highly resistant to biodegradation) whereas there are different fossil-based carbon materials that are biodegradable (e.g. polycaprolactone) [10, 25, 29, 54, 65, 73–75] (Fig. 2).

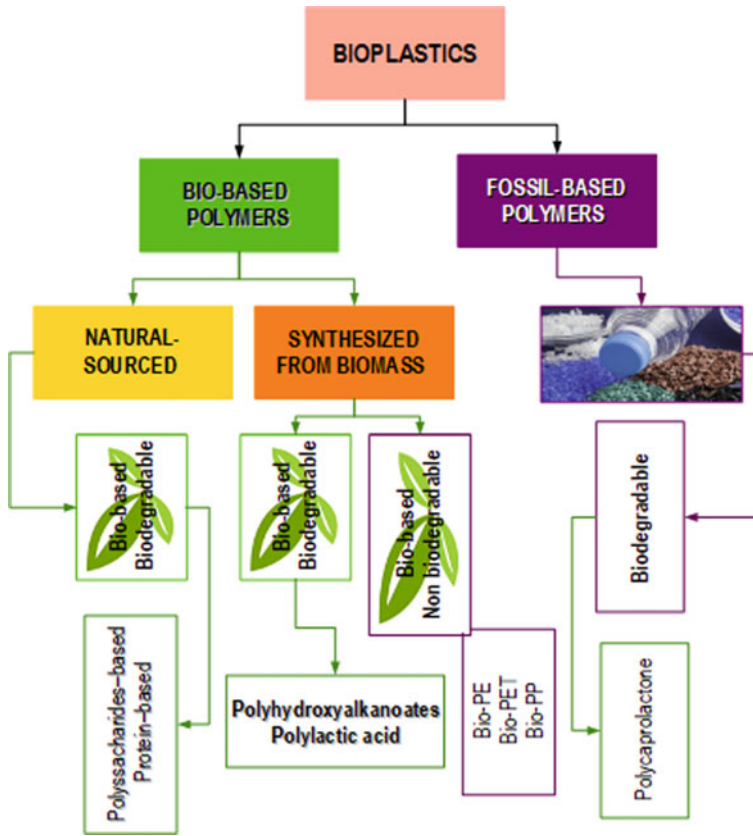


Fig. 2 Segregate of bioplastics into bio-based and fossil-based materials based on biodegradability

2.1 Biodegradation of Biopolymers Under Various Environments: An Overview

Biopolymers are gaining more and more interest owing to their multidimensional characteristics such as bio-based nature and biodegradability/compostability properties [13, 14, 76]. Biodegradability refers to a potentiality of the biopolymers to be completely biodegraded (disintegrated) by biological agents (microorganisms and enzymes in the biosphere) [28, 50, 54]. Biodegradation is a complex chemical/biological activity, biopolymers being completely mineralized by the extracellular enzymes excreted by several microorganisms (especially bacteria and fungi) into natural substances and biomass [13, 14, 29, 31, 46–49, 51–53] (Fig. 3).

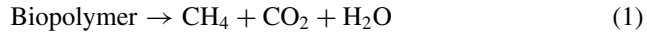
Briefly, biodegradation is controlled by the physico-chemical and biological characteristics of the soil and starts with the adherence of microbial cells to the surface of biopolymer material, the biofilm formation, and the releasing of various chemical substances and numerous extracellular enzymes (esterases and lipases),

Fig. 3 Complete microbial biodegradation of bio-based bag



which fragment the biopolymer material [13, 14, 46, 48, 51, 58, 59, 77, 78]. The enzymes hydrolyze the ester bonds of the long biopolymer chains, resulting in small fragments of low molecular weight (oligomers, dimers, and monomers) or other smaller molecules and microelements. These small fragments are transported into the microbial cells, where can be bioassimilated and further metabolized/mineralized to simple end products and biomass (biotic disintegration) [13, 14, 28, 48, 51, 58, 59, 61, 77, 79, 80]. At the same time, an abiotic disintegration can occur, this phenomenon being strongly controlled by several major influential environmental factors (environmental stress conditions, e.g. high temperatures over 55 °C and material characteristics) [13, 14, 41, 48, 51, 57]. The biodegradability of biopolymers is controlled by several determinants, such as environmental (oxygen content, heat, moisture, pH, UV, redox potential, nutrient availability, time, and salinity in different waters), biopolymer material (physico-chemical structure, chemical composition, size/shape/thickness/surface area, crystallinity, porosity, additives, fillers, and functional groups), and microorganisms (activity, density, and diversity) and not by their resources or their manufacturing process [3, 13, 14, 28, 58–62]. The thicker, the more complex biopolymer formula, the longer the biopolymer's chain, and high crystallinity result in a slow hydrolysis process [28, 48, 60, 80, 81]. The biotic and abiotic processes can also influence each other, physically breaking down biopolymers into monomers leading to increasing the enzymatic decomposition of the biopolymer and accelerating the mineralizing process by microorganisms [13, 46, 51, 82]. The biodegradation process takes place in landfill, soil, water (fresh or marine water), and compost [13, 14, 16]. Generally, biopolymer-based packaging materials are designed for single-use or short shelf life use, than these appear in landfills as waste. In landfill, the anaerobic biodegradation, a complex process due to the inherent heterogeneity of waste, initially occurs under microbial inoculation from digestion reservoirs, the

pH value being between 5.8 and 8.5 [14, 16, 83]. In the next stages, the pH value decreases, while the level of ammonia, sulfates, and volatile fatty acids increases; acidogenesis produces hydrogen; acetogenic fermentation generates acetic acid, carbon dioxide, and hydrogen; and methanogenesis generates biogas, the landfill working as a bioreactor (Eq. 1) [16, 84].



The discarding of biodegradable biopolymers waste to landfills is the least preferred alternative because under anaerobic environmental conditions, anaerobic disintegrate results in GHGs, especially methane (CH_4) (Eq. 1) [13, 85]. The biological aerobic degradation in soil differs even more than in other environments, depending on region, precipitation and climate, season, temperature, water content, organic matter (plant and animal residues), soil texture (sand, silt, and clay distribution), chemical composition and pH values, and microorganisms activity [14, 61]. Biodegradation is strongly influenced by the presence of water, which is of a great importance in the microbial growth on biopolymer material surface and also in the hydrolysis process. The second stage occurs under the action of microorganisms [61]. The environmental conditions which influence the biopolymer biodegradation in the soil and compost are not illustrative for the fresh water (rivers, lakes, streams, and wetlands) and marine water, where abiotic elements (dissolved oxygen content, saltness, pressure, and temperature) and biotic elements (microbial population and vertically structured biological habitat) depend on the depth of the water, season, rainfall, currents, and geographical location [14, 28, 48, 58, 77, 86]. In terms of salinity, there is a decisive difference, the fresh water having a lower salt content [14]. Even in the most biotic regions of the ocean (cold marine environment), the biodegradation process of biopolymers is very different from those in soil or composting environments. The biodegradable biopolymers reveal smaller biodegradation than in the soil and modern landfills, and the biopolymers that disintegrate in aerobic/anaerobic environments will not have the same biodegradation rate in the ocean [28, 48, 58, 86].

2.1.1 Biodegradability of Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are characterized as hydro-biodegradable materials, their biodegradation occurring both aerobically and anaerobically to produce CO_2 , water, and CH_4 in the first case or only CO_2 and water in the second case [13, 87, 88]. Biodegradation of PHAs can take place inside living organisms (resulting in nontoxic metabolites) due to the action of a group of enzymes: intracellular depolymerase (intracellular biodegradation), but also in the surrounding environment (extracellular biodegradation) due to the action of extracellular depolymerase [13, 89–93]. The PHA-biodegrading enzymes (intracellular/extracellular depolymerases and several lipases) are secreted by several microorganisms (especially fungi and bacteria), being able to hydrolyze by a similar mechanism the insoluble PHAs into oligomers and monomers [91, 94–96]. Separately from the action of

intracellular/extracellular depolymerases, the disintegration process is also crucially affected by temperature, microbial populations, availability of nutrients, presence or absence of oxygen, pH, humidity as well as by the conditions of the PHAs biopolymer, including composition, molecular weight, and crystallinity [91, 95]. Further, a smaller surface zone of PHAs materials can limit the microorganism's rise and the longer side chains provide better degradability [95, 97, 98]. PHAs' biodegradability is conversely proportional to the increase in molecular weight, high molecular weight causing a sudden decrease in solubility making them hostile for microbial aggression [91]. Additionally, the copolymers of PHA reveal a superior biodegradation capability than homopolymers, since the surface of copolymers is porous, with low crystallinity, depolymerase hydrolyzing the amorphous part of PHA with more efficacy than the crystalline region [91, 99]. Anaerobic biodegradation of PHA-based biopolymers has different important applications (e.g. medical, agricultural, and packaging sectors), increasing the range of *application* of the PHAs materials [13, 14, 95, 100]. Some of the PHAs include poly-3-hydroxybutyrate [P(3HB)] and poly(3-hydroxybutyrate-co3-hydroxyvalerate) [P(3HB-3HV)], the most famous types of PHAs [14, 62, 101]. [P(3HB)] is a short-length-chain PHA, consisting of units with three–five carbons, the incorporation of hydroxyvalerate into [P(3HB)] resulting in the copolymer [P(3HB-3HV)] [14, 62, 101].

Biodegradability of [P(3HB)]

[P(3HB)] and its blends can be degraded in various natural environments, such as landfill, soil, or water, the soil being an ideal ecosystem for [P(3HB)] biodegradation [14, 91, 102]. [P(3HB)] has a faster anaerobically biodegradation, over 90% being degraded in 10 days in mesophilic conditions [103, 104]. In landfill conditions, the [P(3HB)] biopolymer shows a large biodegradation rate, but its degradation rate in the ocean is remarkably smaller and may even be similar to the biodegradation rate of its fossil-based counterparts [82]. Other older studies that aimed to investigate the biodegradation of [P(3HB)] in landfill found that [P(3HB)] revealed a mass-loss of about 10% (after 13 days, 30 °C) [105], while [P(3HB)] powder showed a mass-loss over 90% after 4 weeks [106], mass-loss being considered an index of biological degradation [107]. Tansengco and Dogma [106] also noted that [P(3HB)] powder had already completely disintegrated after 5 or 7 days by specific bacterial strains. Although biodegradation in landfill is still wanted waste management, due to its advantages, the disposal of bio-based materials waste to landfills continues to be the least desirable alternative but preferable over the uncontrolled disposal [13]. PHAs have been found to be able to degrade the soil environment, the degradation being controlled by the soil, microorganisms' population, the pH of the investigated area, season to season, temperature, humidity, and crystallinity [13, 61, 91, 108, 109]. For instance, the degradability of [P(3HB)] in the soil is hardly temperature-dependent with a mass-loss assigned to the fungal action [109]. Some researchers noted a loss in the mass of granules (5 mm thickness) of 15% and 98% in the case of films, after one year [108]. Other researchers have found that PHAs lost weight after about

12 weeks [75]. The fossil-based plastics waste soiling of waters represents a critical issue today, with large accumulations of plastic waste being identified in the ocean [110]. Biodegradation within waters depends mainly on key environmental factors like the presence of microorganisms, pH, temperature, and nutrients, the rate of biodegradation being higher in the ocean than in fresh water [13]. PHAs, according to Mergaert et al. [111] and Rujnic and Pilipovic [60], are capable to degrade in fresh water and ocean, the size and shape of the [P(3HB)] influencing their biodegradation more than their chemical composition [92]. The biodegradation of [P(3HB)] in fresh water does not differ remarkably from that in the ocean [14, 111]. [P(3HB)] is one of the few plastics highly biodegradable in various ocean environments [14, 93]. The high biodegradability of [P(3HB)] in the ocean environment is related to its degrading microorganisms and some characteristics of depolymerases such as enhanced hydrolytic activity in the ocean environment and stability in the ocean pH range of 7.8–8.2 [93]. PHAs are also biodegradable in sewage sludge, where large bacteria density is advantageous for biodegradation [14, 91, 105, 112, 113]. Nishida and Tokiwa [105] have noted a mass-loss of [P(3HB)] of nearly 30% at 30 °C in sewage sludge after 13 days, while [112] have shown a complete mass-loss at 35 °C for sheets with 0.5 mm thickness after 12 weeks and after 19 weeks for sheets with 3.5 mm thickness. Recently, it has been observed that the [P(3HB)] was degraded in 9 days in the anaerobic sludge [104]. Very recently, the [P(3HB)] films have proven an important biological degradation after 6–10 weeks of exposure to sludge media [102]. A large part of biodegradable materials are compostable, the composting process, one of the most desirable solid waste valorization into homogeneous useful materials, being achieved at both industrial and domestic scales, with the same procedure and resulting products. At least 90% of biodegradable materials can be disintegrated in a controlled composting environment within six months, while a biodegradation of at least 90% of the mass to smaller fractions should take place within three months when in contact with organic materials [13].

Biodegradability of [P(3HB-3HV)]

[P(3HB-3HV)], one of the most used PHAs, is 100% biodegradable in terrestrial and aquatic environments [114–118]. [P(3HB-3HV)] contains short methyl side chains just like [P(3HB)] and ethyl side chains due to its 3-hydroxyvalerate monomer in the polymer sequences. At the same time, the 3-hydroxyvalerate level has a significant positive effect on the [P(3HB-3HV)] biodegradability [14, 90, 118–120]. [P(3HB-3HV)] is one of the few biopolymers which are biodegradable in natural environments, especially in ocean and soil, producing monomers that are further mineralized [14, 115, 120]. In a real landfill, [P(3HB-3HV)] strips with 1 mm thick were fully disintegrated at 20–24 °C after 280 days [121]. [P(3HB-3HV)] has been found to be readily biodegradable in the soil environment [108, 109, 122, 123]. Luzier [122] has reported a total weight loss of strips made of [P(3HB-3HV)] bottles after 525 days. Volova et al. [123] have noted that the [P(3HB-3HV)] biodegradation was

superior than the homopolymer [P(3HB)] under the same circumstances, biodegradation in the soil being influenced by the difference of crystallinity (homopolymer having 65–80% crystallinity and the copolymers 50–65% crystallinity). The [P(3HB-3HV)] copolymer usually has a higher biodegradation rate compared to [P(3HB)] homopolymer, it is attributed to the porous [P(3HB-3HV)] surface morphology, with low crystallinity [124]. Mergaert et al. [109] have shown differences between the biodegradation rates, such as a daily mass-loss of 0.09% (15 °C), 0.14% (28 °C), and 0.64% (40 °C), proving also a faster biodegradability of [P(3HB-3HV)] than homopolymer [P(3HB)]. Recently, Boyandin et al. [108] have observed that 61% of the [P(3HB-3HV)] pellicle is biodegraded, while only 35% of the [P(3HB-3HV)] grains is disintegrated after 365 days. [P(3HB-3HV)] can be hydrolyzed rapidly also in water [14]. Mergaert et al. [109] have shown that [P(3HB-3HV)] with 10 mol% hydroxyvalerate content was disintegrated 77% (a total mass-loss) in fresh water after 358 days, while under the same experimental conditions, the [P(3HB-3HV)] with 20 mol% hydroxyvalerate amount, a total mass-loss was experienced. In fresh water, [P(3HB-3HV)] strips from the bottle (1 mm thick) lost only 29% of their weight after 350 days at low temperatures without providing information on the environmental parameters and [P(3HB-3HV)] composition [121]. The hydroxyvalerate level is an important parameter that influences the [P(3HB-3HV)] biodegradability, Eubeler et al. [125] reporting that [P(3HB-3HV)] with 21 mol% hydroxyvalerate was totally disintegrated in fresh water at 6 °C within 254 days. PHAs are known to be highly disintegrated and mineralized in various ocean environments (e.g. coastal areas, shallow-water, deep-sea environments, and estuaries) [93]. Some researchers have observed a decrease in the thickness of the [P(3HB-3HV)] foils with 100–140 μm after 17 weeks [126] and a decrease in the weight of the [P(3HB-3HV)] foils with 60–65% after 6–8 weeks of environmental exposure [79, 126], the biopolymer surface being rougher [79]. As noted by Rutkowska et al. [79], [P(3HB-3HV)] films having 0.115 mm thickness showed 60% weight loss in seawater within 6 weeks, whereas the composite [P(3HB-3HV)]/[P(3HB)] (60%) revealed only 38% weight loss as degraded in seawater. Environmental exposure of [P(3HB-3HV)] at coastal waters suggested that the [P(3HB-3HV)] biodegradation time is positively influenced by degrading microbial viable cell counts [127]. It also noted that the biodegradability of [P(3HB-3HV)] material in the seawater was considerably influenced by the material parameters (thickness and surface area), being of 13% after 160 days for [P(3HB-3HV)] pellicle with 0.1 mm thick, respectively, 54% for [P(3HB-3HV)] pellicle only 0.005 mm thick [96, 128]. Other researchers found cavities and fractures on the [P(3HB-3HV)] fibers immersed in deep seawater [129]. Recently, the biodegradability of [P(3HB-3HV)] in ocean and submarine soil was experienced as 90% after 210 days exposure [130]. Very recently, it has been also noted that the product parameters had a significant influence on the PHAs biodegradation time, for instance, the time for total disintegration of bags with 0.035 mm thickness being 25 days to 2 months, while for bottles with 0.8 mm thickness being 1.5 years [131]. These researchers appraised a PHAs biodegradation rate of 0.04–0.09 mg/day/cm² and predicted that this degradation rate would take about 1.5–3.5 years to completely biodegrade a [P(3HB-3HV)] bottle 800 μm thick [131].

2.1.2 Biodegradability of Polylactic Acid

PLA-based polymers, an interesting alternative to fossil-based polymers, are used in numerous applications (e.g. food/beverage packaging, agricultural sector, furnishings, hygiene personal products, etc.) [31, 32, 36, 37, 62, 132] and the items based on PLA can be recycled after their end life (either mechanically or chemically) or discarded in the sanitary landfills [32]. However, PLA is extremely little mineralized in most environments such as landfills and ocean environments [28, 37, 61, 82, 133], at temperatures of at least 30 °C, occurring a slow hydrolysis of the PLA ester bonds [134]. Some researchers examined the biodegradation of PLA pellicles with 0.05 mm thickness in the ocean (natural circumstances) and in the laboratory (static circumstances) and noted that the overall PLA properties did not change considerably (after 10 weeks in laboratory circumstances) [135]. Numerous studies in real composting conditions have been recorded [32, 136–138]. In a study by Wang et al. [137], the ammonia influence on the biological degradation of PLA under thermophilic (55 °C) and hyperthermophilic (80 °C) anaerobic exposure was evaluated. They have noted that the PLA transformation in lactic acid was insignificant at 55 °C, while at 80 °C, the PLA was hydrolyzed to lactic acid, the hydrolysis process being increased with ammonia addition and microbial activity. Kolstad et al. [32] explored the behavior of PLA biopolymer in landfill conditions, aiming to obtain details on the anaerobic biological degradation of PLA under circumstances of modest temperature and considerable time (21 °C for 390 days, and 35 °C for 170 days). Their two experiments, conducted under accelerated biodegradation conditions, revealed that the semicrystalline PLA (>96% of resin) did not generate an important amount of biogas, while the amorphous PLA produced a low quantity of biogas at 35 °C. The amorphous part of PLA is easily accessible by microbial population [132], the hydrolysis reactions being initiated in the amorphous regions within the polymer matrix [139]. Kolstad et al. [32] concluded that any degradation of PLA in landfills would demand chemical hydrolysis before any biodegradation. In a work by Yagi et al. [138], various sizes of PLA pellicles (25 mm thick) were used to study the biodegradation at 55 °C in anaerobic sludge conditions, the small pieces of PLA film having a slow rate of anaerobic biodegradation than the large PLA samples. They also showed that the lower activity of sludge led to slower anaerobic biodegradation of PLA film. PLA has been shown to anaerobically biodegrade only 7% in 90 days in mesophilic conditions, while [P(3HB)] biodegraded over 90% in 10 days [104]. Boonmee et al. [140] found that the PLA bottles lost about 90% of their weight in 90 days, at 61 °C in dark conditions. During the biodegradation experiment, the PLA pieces were constantly broken into little brittle units, their dimension being less than 1 mm at the end of the experiment. In addition, the PLA surface revealed many pores, cracks, and irregular roughness. Moon et al. [136] examined the biodegradation of PLA in similar conditions to the outdoor landfill and soil, using anaerobic microorganisms from sewage sludge. The biodegradability of PLA was assessed as specific gas (CO₂ and CH₄) production rates measured after 30 days under aerobic and anaerobic conditions. They concluded that the increase of PLA-specific surface area can lead to an increase in gas production level. PLA biodegradation results in

water-soluble components, which reduces the pH values of soil or compost, negatively influence the farm products, thereby the pH should be controlled. Goto et al. [141] examined the biodegradation of PLA using sub-critical water and noted that the pH value of compost combined with 40% of preprocessed PLA could be directed within pH of 5.4–5.5 over 90 days. The biodegradable biopolymers can also be recycled rather than incinerated, but they reveal a loss in physico-mechanical properties, besides [P(3HB-3HV)] that can be recycled up to five times less loss in physical properties [52, 142]. However, recycling is an expensive and energy-rigorous treatment [10, 17].

3 Carbon Footprint and Climate Change: An Overview

The Carbon Footprint (CF), a significant current megatrend, refers to the indirect GHGs particularly CO₂, CH₄, and nitrous oxide (N₂O) resulting from the life cycle of the polymer-based product (resources extraction, refining and manufacturing, distribution, use, and end-of-life) or biopolymer-based product (bio-sourced rise, raw material harvesting, biomass processing prior to bio-refining, fermentation, purification, subsequent injection or blow molding, transportation, use, and end-of-life choices) and their sustainability, CO₂ being a large driver of global climate change [3, 4, 15, 18, 43, 78, 143–146]. Climate change is contributing to profound changes within the global level, which is being often seen as a stress factor that puts pressure on the global systems and is recognized as an imperative concern for this period [147, 148]. A major source to GHGs is the polymer-based packages (40% of polymers being used as packaging materials), from the oil extraction and transportation (12.5–13.5 million metric tons of CO₂ equivalent per year) manufacturing, use, to the package end-of-life (91 million tons of GHGs by 2050 if plastics manufacturing and incineration increase; a 22% increase from the baseline), *polymers packages* being among the *most* carbon-intensive materials [149]. Incineration is the significant starting point of GHGs, the emissions generated by incineration being higher than the emissions by landfills, even if the most plastic waste ends up in landfills (58%) [43, 149]. The bio-based biodegradable biopolymers sector has the potential to reduce global warming potential (kg CO₂ equivalent per kg of polymer/biopolymer), being approximated that replacing 65.8% of the world's petroleum-based materials with bio-based biodegradable materials would escape 241.316 MtCO₂-equivalent (CO₂e) yr⁻¹ [43, 149, 150]. To reduce GHGs from petroleum plastic packages, the petroleum plastic packages can be replaced with bio-based biodegradable packages, which contribute to the process of industry de-carbonization, due to lower levels of GHGs than their petroleum plastic counterparts [8, 10, 15, 21–28, 43, 149, 151]. Thereby, the GHGs of PLA are only 0.5 CO₂ equivalent per kg of PLA, being roughly a 75% reduction in CF versus the most conventional petroleum-based plastics [15, 152] (e.g. GHGs of polypropylene are 1.91 CO₂ equivalent per kg; polyethylene –1.98 CO₂ equivalent per kg; polyethylene terephthalate –2.94 CO₂ equivalent per kg; polystyrene –3.68 CO₂ equivalent per kg; polyurethane –5.70 CO₂ equivalent

per kg). In point of the use of pure PHAs and PLA for carbonated beverage bottles is restricted due to the unfavorable properties (poorer gas and moisture barriers, thermal and mechanical characteristics, low chemical and low heat resistance, as compared to the petroleum-based materials); therefore, blending of PHA with PLA, cellulose derivatives, lignin, starch, and various nanoparticles may efficiently modify the PHA and PLA stability, as well as their barrier, mechanical, and thermal properties [62, 153]. The GHGs of PHA and PLA may fluctuate depending on the category of blending material and the reinforcement nanoparticles; overall, the environmental impact of PHA blending can be lower than that of the PLA blending [152]. Biodegradable bio-based plastics are designed to be disintegrated in industrial composting conditions that are also a source for GHGs (CO_2 , CH_4 , and N_2O), being dominated by CO_2 emissions. The total CO_2 equivalent releasing for biopolymer composting is large (average 1.62 kg CO_2 equivalent/kg of biopolymer) when compared to mechanical recycling (0.32 kg CO_2 equivalent/kg of material) and landfilling (0.03 kg CO_2 equivalent/kg of biopolymer), but smaller when compared to incineration (2.71 kg CO_2 equivalent/kg of material).

4 Conclusions and Future Scope

The numerous problems associated with the environmental adverse influence of fossil-based plastics result in switching from non-biodegradable petroleum-based polymers to greener biodegradable polymers that have the potential to solve fossil-based waste pollution, due to their biodegradability, a major and undeniable advantage. They are disintegrated into natural substances and biomass once they end up in the environment and do not produce harmful substances during mineralizing. The biodegradation of biopolymers depends on numerous factors, such as the environment (landfills, soil, fresh water, ocean, and home compost, industrial composting plants), intrinsic biopolymer material characteristics, and microbial action. In landfills, the anaerobic disintegration occurs slowly, firmly depending on the working conditions. The disposal of bio-based biodegradable plastic waste to landfilling is the least suitable way but preferred over the uncontrolled discharge. The biodegradable plastics, especially polyhydroxyalkanoates, have been found to be able to degrade in the soil environment, the rate of biodegradation being strongly dominated by the presence and temperature of microorganisms. Polyhydroxyalkanoates also undergo ocean degradation in acceptable time but show slower biodegradation rates than in the soil and modern landfills. Polylactic acid is extremely little mineralized in most environments, it is compostable only in industrial composting conditions, actually the industrial composting represents the most advantageous biodegradation strategy. The second major advantage of bio-based biodegradable plastics is their ability to reduce GHGs and carbon footprint compared to petroleum-based plastics. The bio-based biodegradable polymers can also concur to climate change mitigation by refraining from the fossil-based feedstock. It should be mentioned that the problems associated with fossil-based plastics (especially fossil-based plastic waste) are not solved

just by switching to bio-based biodegradable materials, and stricter regulations and encouraging eco-friendly behavior are needed.

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Biopolymers: Regulatory and Legislative Issues



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Abstract The European Green Deal is working towards zero waste and pollution through the well organized use of natural resources, as obtaining and disposing of conventional polymer-based materials is considerably challenging in this respect. With the negative influence of conventional polymer-based materials on the environment and climate change (greenhouse gases emissions, particularly carbon dioxide emissions; waste; leakage in biosphere; incineration with a strong negative environmental influence through carbon dioxide) the use of bioplastics has become a top priority. In the development and adoption of biological degradable and compostable materials, the standards and regulatory aspects are an important driving force. This chapter offers an overview of the important standards used to assess the biodegradability and compostability of biopolymers, and discusses some aspects related to potential migration from biopolymer-based formulations. The data presented in this chapter can be useful for researchers who want to develop and adopt bioplastics.

Keywords Zero waste · Bioplastics · Biodegradable · Compostable · EN 14,995:2007 · EN 13,432:2001/AC:2005 · ISO 17088:2012 · ASTM D6400-12 · Migration · European Regulation 10/2011

1 Introduction

The European Green Deal aims at modifying the European economy into an well planned, clean and sustainable economy by the efficient use of natural sources, and stopping the climate change, reverting biodiversity damage, and reaching zero waste and pollution [23, 57]. In this frame of reference, bioplastics are regarded as one strategy to afford major circularity in the packaging industry, and go on a low-carbon economy. Bioplastics or biopolymers, which can be classified into three categories consisting of bio-based and biodegradable materials, just bio-based and just

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biodegradable materials [23, 92] (Table 1), have been the focus of a lot of debate at international level for some time now [23].

The *bio-based* term refers to the agro-based raw (renewable) materials predominantly used to produce plastics, while the *biodegradable* term addresses to the potentiality of the materials in question to be completely degraded by the microbes in the environment, which assimilate the bio-based material as a food source, bio-based materials being not necessarily biodegradable [1, 32, 35, 39, 50, 83, 95, 97, 98, 113, 116, 117]. In a greater appropriate way, biodegradable/compostable bioplastics are bio-based materials that comply with the approved standard test protocols of biodegradability and compostability, respectively. Standardization processes exist at different levels (national/continental/international), a number of continental and international harmonized norms comprising protocols to claim biodegradability and compostability being available [23, 35]. The principal international/continental/national organizations that have set standards are ISO (International Organization for Standardization) [51], ASTM (American Society for Testing and Materials) [42], CEN (European Committee for Standardization [46], DIN (German Institute for Standardization) [47], BSI (British Standards Institution) [45], JSA (Japanese Standards Association) [54], OECD (Organization of Economic Cooperation and Development) [55], and AS (Standards Australia) [56]. When assessing the environmental capacity of bioplastics, the main centre of attention is placed not only on the end of life but also on the performance during the use phase (e.g. chemical migration from bioplastics) [120]. Compounds intentionally added in bioplastics formulation can be transferred to air, solids, or liquids, bioplastics being a significant source of chemical exposure to humans and potentially also to different

Table 1 Illustrative examples of bioplastics

Categories of bioplastics	Examples	References
Bio-based and biodegradable	PLA (polylactic acid) PHAs (polyhydroxyalkanoates) Bio-PBS (polybutylene succinate) polysaccharides-based (starch, cellulose, gums, pectin) protein-based (chitin/chitosan, keratin)	[3, 5, 20, 30, 33, 34, 36, 39, 80, 81, 85, 90, 92, 95, 96, 100, 103–107, 110, 111, 117, 118]
Only bio-based	Bio-PP (bio-polyamides) Bio-PE (bio-polyethylene) Bio-PET (bio-polyethylene terephthalate)	
Only biodegradable	PCL (polycaprolactone) PVA (polyvinyl alcohol) PBAT (polybutylene adipate terephthalate)	

environments [38, 88, 120]. This chapter aims to offer an overview of the significant standards that are in place to assess the biodegradability and compostability of bioplastics. In addition, some aspects related to migration are also reviewed.

2 Significant Standards for the Biodegradability and Compostability of Bioplastics

A standard is a document approved by an established body and offers regulations, instructions and characteristics for a product, process and method of the product obtaining [52]. In this sub-section, emphasis will be laid only on ISO, ASTM and EN standards, which can be connected to the biological degradability and compostability of biopolymers or bioplastics. Bioplastics undergo the same standard test protocols as conventional plastic materials [44]. A number of international and European standards regarding biodegradability and compostability are available online (Table 2). At the international level, ISO provides a number of standards regarding biodegradability in different environments (aqueous medium, marine sediment, seawater, seawater/sediment interface, soil, sludge), and compostability [31, 53]. ASTM provides a lot of standards referring to biodegradability in different environments (landfill, marine environment, soil) and compostability [43], while CEN has issued a series of standards (CEN addresses to the ISOs) significant for the biodegradability, compostability of bio-based plastics [31, 41] (Table 2).

As stated by ASTM, biodegradable plastics are the plastics that can be degraded by some microbial cells consisting of bacterial and fungal cells, and algae [49], but a buyer can observe that a material is biodegradable if there is a label on that material, the usually standardized labels being offered by the certification institution such as TÜV Austria and DIN CERTCO. DIN CERTCO describes the biodegradability class [31]. Regarding biodegradability and compostability, the label is based on a number of crucial norms of significance for the compost environment (e.g. [11, 23, 26, 27, 31, 71, 99]). The EN 14,995:2007, EN 13,432:2001/AC:2005, ISO 17088:2012, and ASTM D6400-12 standards express that some criteria must be considered for a material to be compostable, such as material composition, disintegration, biodegradation and composting [29, 48]. EN norms stipulate that the organic content deemed as volatile solids must be at least 50%, while ASTM D6400-12 norm does not specify a threshold level of organic content; in addition ASTM D6400-12 allows higher levels for heavy metals than the EN norms [23]. EN standards specify that at least 90% of the initial dry weight disintegrates into particles (less than 2 mm in size) after 12 weeks, while ASTM D6400-12 and ISO 17088:2012 stipulate that the disintegration takes place after 45 days (even up to six months-ISO 17088:2012) [29, 48]. The EN 13,432 norm is the most strict of all of the norms for the assessment of the biodegradability and compostability, providing assessment criteria to see if the various materials can be biodegradable and compostable [40]. For aerobic biological degradation, the EN 13,432:2012, EN 14,995:2006, and ISO 17088:2012 norms stipulate that a 90% level

Table 2 ISO, ASTM and EN standards of biodegradability and compostability

Standards	Headline	References
ISO 23517:2021	This norm describe the test protocols and assessment criteria through address the verify of components, biological degradation, and negative influence on earthly organisms, being appropriate to biological degradable plastics used to obtain mulch membranes or biological degradable mulch membranes set to be used for mulch implementation in farming and horticulture	[77]
ISO 16929:2021	The ISO 16929:2021 standard takes part in the protocol for the assessment of the industrial compostability of plastic materials as specified in ISO 17088 standard. The ISO 16929:2021 establishes the protocol used to set the disintegration level of plastics in a pilot-scale aerobic composting test under exact procedure. The protocol formulated in ISO 16929:2021 is also used to evaluate the impact of the test material on the composting treatment and the quality of the finished compost	[70]
ISO 23977 1:2020	Biological degradation is found by measuring the CO ₂ level developed from plastics exposed to seawater in coastal regions. The conditions in ISO 23977 1:2020 might not every time correlate with the most favourable conditions for the maximum level of biological degradation, nonetheless this norm is designed to offer an indicator of the potential biological degradability of plastics	[78]
ISO 23977–2:2020	Biological degradation is highlighted by measuring the O ₂ request in a closed respirometer device from plastics displayed to seawater in seaside regions. The settings included in ISO 23977 2:2020, in the same way as those described in ISO 23977 1:2020, might not every time correlate with to the most favourable settings for the highest level of biological degradation; nonetheless this norm is outlined to offer an indicator of the probable biological degradability of plastic materials	[79]
ISO 22404:2019	This standard is designed to assess of the aerobic biological degradation of non-floating plastics revealed to aquatic sediment through analysis of released CO ₂ . Biological degradation is highlighted by measuring the CO ₂ level developed from plastics exposed to marine sediments from eulittoral region	[76]
ISO 16929:2019	The ISO 16929:2019 takes part of the protocol for the evaluating of the compostability of plastis as highlighted in ISO 17088. This norm is also used to test the material effects on composting and the quality of the finished compost	[68]

(continued)

Table 2 (continued)

Standards	Headline	References
ISO 13975:2019	The ISO 13975:2019 norm describes a protocol of assessment of the anaerobic biological degradation of plastics in a supervised anaerobic sludge digestion equipment with a solids level not surpassing 15%. The protocol is developed to give an amount of transformation of the organic carbon from plastics (e.g. polymers, copolymers, water-soluble polymers) to CO ₂ and CH ₄	[60]
ISO 14855-2:2018	This standard is designed to assess of the aerobic biological degradability of plastics under exact composting settings through analysis of released CO ₂ . This standard designed a protocol to give the best rate of biological degradation by reshaping the conditions of the composting equipment (humidity, aeration, temperature)	[65]
ISO 14852:2018	The ISO 14852:2018 is designed to evaluate the aerobic biological degradability of plastics in an aqueous medium through analysis of released CO ₂ . This norm allows the assess of the biological degradation to be enhanced by counting a carbon balance	[62]
ISO 19679:2016	This standard provides a protocol to evaluate the level of the aerobic biological degradation of plastics exposed to different seawater/sediment-zones (sublittoral region) by measuring the released CO ₂	[74]
ISO 18830:2016	The ISO 18830:2016 is designed to provide a protocol to evaluate the level of the aerobic biological degradation of plastics exposed to marine sandy sediments at the demarcation line seawater-seafloor, by quantifying the O ₂ request in a sealed respirometer device	[73]
ISO 14853:2016	This norm depicts a protocol test for the evaluation of the anaerobic biological degradability of plastic materials in an aqueous system by anaerobic microbial cells	[63]
ISO 20200:2015	The ISO 20200:2015 norm is not appropriate for the assess of the biological degradability of plastic materials under composting conditions, additional testing being required to be able to assert compostability	[75]
ISO 15985:2014	The ISO 15985:2014 norm is devised to report the level of carbon from material and its rate of transformation into released biogas (CO ₂ , CH ₄)	[66]

(continued)

Table 2 (continued)

Standards	Headline	References
ISO 16929:2013	The ISO 16929:2013 norm is a piece of an all-inclusive protocol for the assessment of the compostability of plastic materials as profiled in ISO 17088 norm. This standard can also be used to evaluate the effect of the material on the composting treatment and on the quality of the finished compost	[67]
ISO 17556:2012	The protocol test depicted in the ISO 17556:2012 standard is designed to give an optimum level of biological degradation which takes place in a natural environment	[72]
ISO 17088:2012	This standard depicts the similar test protocol as EN 13,432:2001, EN 14,995:2007, and ASTM D6400-12 documents	[71]
ISO 14855-1:2012	The ISO 14852:2018 is designed to evaluate the aerobic biological degradability of plastics under exact composting settings (for the organic fraction of solid mixed municipal waste) through analysis of released CO ₂	[64]
ISO 13975:2012	This ISO 13975:2012 international standard describes a protocol of assessment of the anaerobic biological degradability of plastics in a directed anaerobic sludge digestion equipment with a solids level below 15%	[59]
ISO 10210:2012	This standard depicts the protocol used in the evaluation of aerobic/anaerobic biological degradability of plastics exposed to aqueous medium, anaerobic digesting sludge, controlled compost and soil	[58]
ISO 14851:1999	This norm specifies a protocol for the evaluation of the level of aerobic biological degradability of plastics (as well as those that contain formulation additives) exposed to an aqueous medium through measuring the O ₂ request in a closed respirometer equipment	[61]
ASTM D5338-15(2021)	The ASTM D5338-15(2021) norm provides the protocol for determining the level of aerobic biological degradability of plastics placed in exact composting settings, being equivalent to the ISO 14,855 norm	[6]

(continued)

of biological degradation has to be obtained within six months, while the biological anaerobic degradation time must not be longer than two months. The ASTM 6400–12 norm sets a less rigorous limit of 60% biodegradation (within six months for homopolymers/random copolymers), and 90% biodegradation (within six months for copolymers/polymer blends) [29]. Related to composting, the EN 13,432:2001

Table 2 (continued)

Standards	Headline	References
ASTM D6954-18	The ASTM D6954-18 guide is used on three levels (abiotic processes, measuring biological degradation, evaluation of ecological effect of the products resulted from abiotic processes, and biodegradation) for expediting and quantifying the loss in molecular weight and other properties by thermal and photooxidation processes. There is no ISO norm that corresponds to the ASTM D6954-18 guide	[14]
ASTM D5988-18	The ASTM D5988-18 norm is designed to determine the level of aerobic biological degradation by measuring the released CO ₂ from the plastics revealed to soil, being similar to the ISO 17556 standard	[10]
ASTM D5929-18	This norm offers a simulation of the overall composting process, keeping reproducibility	[9]
ASTM D5526-18	The ASTM D5526-18 norm is devised to give a level of carbon transformation from sample to gaseous carbon under conditions that resemble the conditions found in landfills. There is no ISO standard equivalent to The ASTM D5526-18 standard	[8]
ASTM D5511-18	The ASTM D5511-18 norm is designed to give a level of carbon transformation from sample to gaseous carbon under conditions found in high-solids anaerobic digesters, treating municipal solid waste and biologically active landfills, being equivalent to ISO 15,985 norm	[7]
ASTM D6868-17	This norm describes the requirements for labelling materials (as well as packaging materials), where a biodegradable plastic-based membrane or coating is fixed to a compostable substrate and the whole package is developed to be composted in municipal and industrial composting equipments. Nevertheless, this norm does not depict the package performance related to compostability or biodegradability	[13]
ASTM D6691-17	This standard is projected to index the polymers that are probably biodegradable, relative to a positive reference material, in an aerobic environment. There is no ISO standard equivalent to the ASTM D6691-17 standard	[12]
ASTM D7473-12	The ASTM D7473-12 norm is used to evaluate the weight loss of non-floating plastics incubated in marine aquarium conditions (characteristic of the aquatic environment close to coasts and the bottom of the water body in the absence of sunlight, especially UV-light. There is no ISO standard corresponding to the ASTM D7473-12 standard	[15]

(continued)

Table 2 (continued)

Standards	Headline	References
ASTM D6400-12	This norm overlaps the plastic materials developed to be composted in municipal or industrial equipments, and establishes if the plastic materials are reasonably composted in municipal/commercial composting equipments	[11]
ASTM D7475-11	The standard is a modification of the ASTM D5526-18 norm (it refers only to anaerobic degradation), being used to evaluate the level of aerobic/anaerobic degradation, biological degradation of plastics in a bioreactor landfill test environment, simulating the change from aerobic to anaerobic environment over time as the landfill depth increases. There is no ISO standard corresponding to the ASTM D7475-11 standard	[16]
prEN 17,427:2020	The prEN 17,427:2020 standard is designed to develop a testing protocol for the carrier bags made of any materials that are considered to be appropriate for use in well-managed home composting installations run by householders for personal uses	[99]
EN 17,033:2018	This norm stipulates the demands for biodegradable films (in soil) made of thermoplastics, to be used for mulch applications in farming and horticulture	[28]
EN 14,995:2007	This norm stipulates the protocols to evaluate the compostability/anaerobic treatability of plastic packaging materials (in general) based on biodegradability, disintegration in the course of biological treating, impact on the biological treating operation, and impact on the final compost	[27]
EN 13,432:2001/AC:2005	<i>Packaging—Requirements for packaging recoverable through composting and biodegradation—Test scheme and evaluation criteria for the final acceptance of packaging</i> /This norm stipulates the protocols to evaluate the compostability of packaging materials based on biodegradability, disintegration in the course of biological treating, impact on the biological treating operation, and impact on the final compost	[26]

and EN 14,995:2007 standards describe the anaerobic biodegradation protocol. The level of biodegradation (measured by the generation of biogas) must be at least 50% after a period of two months as anaerobic fermentation is followed by aerobic fermentation, during which the biological degradation can go on. The EN 14,995:2007, EN 13,432:2001/AC:2005, ISO 17088:2012, ASTM D6400-12 norms specify that after a period of specific time (five weeks: EN 14,995:2007, EN 13,432:2001/AC:2005) of anaerobic/aerobic process, at most 10% of the initial dry weight may retain after filtering through holes more than 2 mm in size [48].

3 Migration Concerns

Bioplastics are viewed as a sustainable substitute to petroleum-based materials [87, 120]. From an environmental point of view, biopolymers are an excellent alternative for the food/beverage packaging eco-design. Nevertheless, the use of pure biopolymers is restricted because they have inadequate physico-chemical features, such as low diffusion (water, gas) barrier, lower chemical stability, insufficient mechanical and thermal properties and insufficient long-term stability, than their conventional fossil-based counterparts [101, 108]. These inadequate physico-chemical features can be improved by more additives (e.g. carbon nanotubes, chain initiators, cross-linking compounds, monomers, oligomers, other biopolymers, natural fibres, nanoparticles, nucleating agents, plasticizer molecules, stabilizers, etc.) added into the biopolymer formulations, which can provide supplementary functions to bio-based packaging materials [19, 101, 102, 109, 120]. Packaging materials bring a decisive contribution to the quality and safety of food/beverage products. Possible interactions can occur not only between the packaging material and the food/beverage inside it, but also between the packaging material and the external environment, which can be unfavourable to food and the external environment, respectively [109, 114]. The possible interactions which can take place in the package–food/beverage–environment system refer to permeation, migration and scalping/absorption [104, 109]. Migration consists of the transfer of some compounds from the biopolymer-based packaging material to the interface between the biopolymer, and either the food/beverage matrix or the external environment, thereupon these are released into the respective medium [24, 109] (Fig. 1).

Biopolymers, like all conventional polymers, can contain monomers and oligomers (e.g. lactic acid monomer, lactide acid cyclic dimer, polyhydroxyalkanoates' monomers) [2, 4, 17, 22, 37, 83, 86, 89, 91, 94, 108, 115, 119], which can migrate in the same way as the additives embedded to enhance the physico-chemical characteristics of the biopolymer matrix. The oligomers can be generated during synthesizing or storage, their formation being influenced by several phenomena which have an effect on biopolymer stability (moisture, contact with aqueous food, thermal processing, ageing process) [112]. Biopolymer, by definition, is frail over time being susceptible to biodegradation/disintegration (their structure evolving over time) [84]. The stability of the biopolymer-based packages (respecting the food shelf-life) is a significant challenge for the food packaging area, avoiding the environmental conditions that trigger the package's biodegradation being crucial [91]. Biological degradation process must be blocked in time of storage, and should exclusively initiate after disposing of the packages [82, 108]. From a food safety standpoint, and in the absence of proper rules dedicated to biopolymer-based materials for food-contact setting, these materials are under the control of the EC (European Commission) 10/2011 [25], in the same way as conventional polymer materials [84, 101, 112]. The European Commission [25] establishes the safety claims of plastic materials, classifying every substance approved for the conventional and biodegradable materials manufacturing, describing the detailed tests for overall and specific

Fig. 1 Possible migration in bio-bottle/beverage/external environment system



migration [101]. Lactic acid is on the document of approved monomers and other beginning chemical compounds in EC 10/2011 with no specifications or restrictions [25, 101, 112], while the cyclic lactide and linear/cyclic oligomers of PLA are not on this document [101, 112]. Likewise, lactic acid is confirmed as a GRAS (Generally Recognized as Safe) food ingredient of FDA (Food and Drug Administration), and there are no comments related to oligomers of PLA [21], as these are not specifically regulated. The oligomers of lactic acid/poly(lactic acid) can migrate into the food matrix and so can pose a risk to the consumer [112]. In the case of PHAs, the migration is also a complex concern, the additives or monomers used for manufacturing PHAs-based packages may not be normally used in plastic-based food packages. Even if the most prominent polymerizates in PHAs [poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate)] are non-toxic, there is a request for more data related to the potential migration and the PHAs behaviour during either manufacturing or biodegradation [91]. As stated by the European Regulation, the oligomers' migration limit should not exceed $0.01 \mu\text{g} \times \text{g}^{-1}$, the oligomers not being on the list of authorized substances [25]. In view of food packaging setting, the potential migration of nanofillers from bionanocomposites into foods is also a complex preoccupation to be taken into account for packaging uses, as nanofillers have a higher capacity for migration [91, 101, 108–110]. The European Regulation also establishes on a case-by-case basis the use of nanoparticles as food package

additives, nanoparticle migration being below the generic migration limit of $60 \text{ mg} \times \text{kg}^{-1}$ [25]. Furthermore, (i) if the biopolymer-based materials are used as edible films/coatings, these should be categorized as food additives; (ii) the protein-based edible films that might include allergens should be mentioned on the food label [93].

4 Conclusions and Future Scope

European economy is moving towards zero waste and pollution, low-carbon, resource-efficient, sustainable and circular economy, the manufacturing and disposal of plastic-based materials being a significant part of this exercise. From this perspective, the adoption of bioplastics seems to be an excellent plan of action aimed at moving towards a sustainable and circular economy. Bioplastics are materials which must comply with the standards of biodegradability and compostability, the standard and regulatory aspects related to bioplastics being an important instrument for their development. Bioplastics' biodegradability and compostability are based on pivot standards such as EN 14,995:2007, EN 13,432:2001/AC:2005, ISO 17088:2012, and ASTM D6400-12, which stipulate the criteria that must be considered for a material to be compostable (e.g. material content, disintegration, biodegradation, composting). When evaluating the biodegradability of bioplastics, attention should not only be drawn on the end of life, but also on the potential transfer of some compounds from the bioplastic formulations to air, solid, liquid environments, during the use and storage phases. The potential migration has a decisive contribution especially to the quality and safety of packaged foods. The structure of biopolymers evolves over time, their stability with respect to the food's shelf-life being a greater test for the food packaging industry. Bioplastics and also bionanoplastics, from a food safety standpoint, are under the control of the European Regulation 10/2011, in the same way as conventional polymer materials.

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Sustainable Green Methods for the Extraction of Biopolymers



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Abstract Plastics have contributed to increased pollution levels in recent years, and their prolonged decomposition creates significant environmental issues. It is time to get rid of these products and look for more ecofriendly alternatives. Biopolymer research is aimed at making the planet more sustainable and green, with a less environmental impact. Biopolymer may be totally or partly biologically based and is generated from sources of carbon biomass like plants, microbes, and animal-based products. In comparison with polymers based on petroleum, biopolymers are less damaging to the environment. In this book chapter, an introduction about biopolymers is given and then their sustainable green extraction, recent developments, and applications are discussed.

Keywords Biopolymers · Green · Pollutant · Environment · Sustainable · Extraction

1 Introduction

Biopolymers are abundantly found in the living beings including plants animals and microorganisms. These materials are significant in a variety of fields because they have unique structures and properties that are not seen in conventional synthetic polymers [177]. The word biopolymer is often used to refer to an organic

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polymer produced organically by living organisms, which exhibit characteristics such as strength, stability, and flexibility [8, 14]. Biopolymers are complex organic compounds made up of monomeric repeating units linked via covalent bonds and utilized to make biocatalysts [93, 196]. These are employed in the green manufacturing of different nanoparticles (NPs) by performing as stabilizers and reducers in aqueous conditions [185]. Bio-based polymers of the first generation were concentrated on polymers that are extracted from agricultural feed stocks, such as corn, potatoes, and other feed stocks for carbohydrates. Furthermore, in current years, the focus has changed due to a need to shift away from capital dependent on food and essential biotechnology breakthroughs [18].

Biopolymers are merging as smart materials with immense industrial applications [259]. Naturally occurring biopolymer nanofibers (cellulose, chitin, etc.) constitute a major contributor to natural materials' exceptional functions and mechanical qualities [100]. While there are many avenues for progress toward a more sustainable future, biopolymer development provides a platform that fits into the paradigm of attaining an ecofriendly environment while decreasing our dependence on fossil fuels. Biopolymer end-products have benefited from recent technical advancements, allowing them to reach greater uses and, eventually, match the performance of synthetic polymers derived from petroleum [81]. Biopolymers derived from plant materials and microbes that can be produced endlessly would create a sustainable industry since they are sustainable, carbon-neutral, and constantly renewing. The successful use of biopolymers and the prospect of developing more complex green materials with a lower carbon footprint promise well for the future design and development of ever-more sophisticated green materials [261].

2 Sustainable Green Extraction of Biopolymers

Conventionally made commodity plastics have recently seen an increased push to be replaced by biodegradable polymers, which have shown to be cheaper and have comparable mechanical characteristics [182, 282]. "Green electronics," "dye," and "heavy metal removal," as well as "oil/water separation," "medicinal agent delivery," "tissue engineering scaffolds," "biological devices," "optics," and "sensing" are just a few of the significant and quickly expanding uses for natural biopolymer materials [167].

2.1 *Green Extraction of Biopolymers of Plant Origin*

2.1.1 Extraction of Cellulose-Based Biopolymers

Cellulose is one of the world's most common and widely available polymers [208]. Cells are the most essential structural component of plant cell walls, which are made

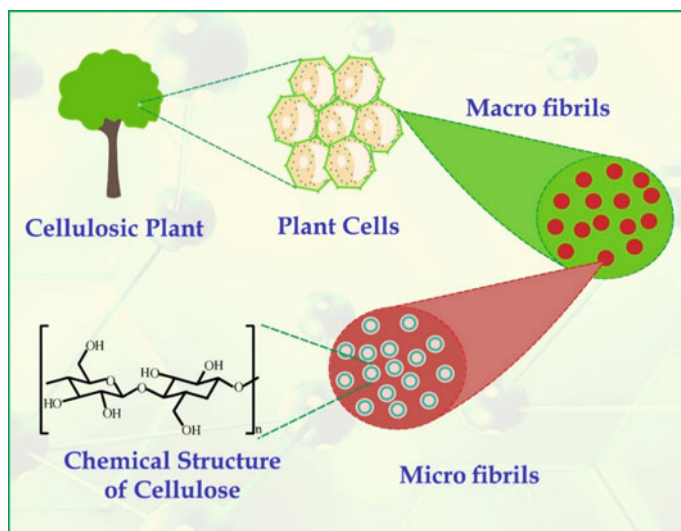


Fig. 1 Schematic representation of cellulose in plant cells and its chemical structure

out of cellulose. This is present in the form of micro fibrils that are little fibrous structures, with each synthase complex having one synthetic unit/glucan series plus a catalytic unit (Fig. 1). Several bacterial species, algae, and fungi also produce it [53, 130, 162]. A bio-based future and a sustainable economy are made possible by cellulose, which is abundant in nature and has a hierarchical fibrous structure, mechanical flexibility, and the capacity to be modified with chemicals. Cellulose also has excellent biocompatibility, renewability, and abundance [295]. Cellulose is a renewable natural fiber that has sparked a lot of research and has emerged as the best and most promising contender to replace synthetic fibers. Trees, plants, tunicate, and bacteria are all the origins of cellulose, which is one of the world's most plentiful and renewable sources of biopolymer materials [30]. On the micro and nano scale, cellulosic fibers have the potential to take the place of synthetic fibers as reinforcement in an ecofriendly green product. In the realm of plant products, cellulosic nanocomposites are one of the most promising fields of scientific and technological development [1]. Bacterial and plant cellulose have similar chemical formula and structure which consist of a homopolymer chain of poly- β -(1,4)-D-glucopyranoside that are connected by β 1-4-linkages [157]. Cellulose is well recognized as a dietary fiber with no upper limit on the amount that may be consumed in food, and it has been shown to modify digest content and have a favorable influence on gastrointestinal physiology and gut microbiota [189]. Various natural fibers, as well as agricultural and marine biomass by-products, have been recently discovered as renewable sources for the production of cellulose. Crop residue accounts for more than half of all biomass produced on the planet. These agricultural wastes represent new territory for cellulose-rich materials like cellulose microfibrils (CMF), cellulose nanocrystals (CNC), and cellulose Nano fibrils (CNF). CNFs are extracted from a variety of plant

derivatives, primarily cotton, banana, rice, and wood pulp. CNF extraction also uses algae, bacteria, and fungus as a starting material [121, 209].

Trees are renewable and sustainable resources that provide us with shelter, oxygen, and help to emit CO₂ from the environment as well as provide natural biopolymers [296]. Tajik et al. [268] used *Sesbania sesban* to extract natural cellulose and create a biodegradable micro composite. A novel iron Schiff base with a min activity was immobilized on cellulose using 2-hydroxy-1-naphthaldehyde as a ligand. In a study published in 2017, Rohani et al. [228] extracted cellulose from rice husk using sodium 30-tungstoptentaphosphate, a green and effective solid acid, resulting in Preysslerheteropolyacid-cellulose acetate hybrid nanofibers. Cui et al. [50] synthesized Nanocrystalline cellulose (NCC) from wheat microcrystalline cellulose using an ecologically friendly ultrasonic-assisted enzymatic hydrolysis method. Under the ideal conditions of 120 h of hydrolysis followed by 10 min of ultrasonic treatment, the NCC yield was 22.57%. In a study, [2] used an autoclave-based and ultrasonication pretreatment to substitute the non-green chlorite extraction approach. Ultrasonic treatment with hydrogen peroxide created 49% cellulose. Ndruru et al. [186] extracted cellulose from *Heobroma cacao* L. (TCL) using a microwave-assisted extraction (MAE) technique that was both efficient and ecologically benign. Cladophora cellulose (CC), produced from green algae, offers unrivaled benefits over other celluloses due to its high crystallinity, low moisture adsorption capacity, excellent solution processability, high porosity in the mesoporous zone, and concomitantly high specific surface area [295]. Jmel et al. [112] extracted cellulose from green macroalga *Ulva lactuca*, a plentiful but underused macroalga that causes eutrophication and other ecological problems. There were no Hemicellulosic pollutants identified, indicating that the extraction procedure was effective. The sustainable manufacturing of Nano Cellulose continues to be a challenge because of biopolymers' low solubility and challenging processability utilizing conventional hazardous solvents. The use of Ionic Liquids (ILs), which has sparked a lot of attention as strong "green" solvents for biopolymer processing in recent years [92]. IL's ionic character is thought to be responsible for the degradation of biopolymers by cleaving hydrogen bonds between cellulose strands [206]. Sun et al. [262] fully dissolved southern yellow pine and red oak in the ionic liquid 1-ethyl-3-methylimidazolium acetate ([C₂mim]OAc) after moderate grinding to extract cellulose. Researchers have recently been interested in cellulose nanocrystal as a possible filler that can overcome the limitations of biopolymer films [182].

2.1.2 Extraction of Lignin-Based Biopolymers

Lignin is a complex biological molecule that is well-known as the world's second most prevalent biopolymer [248]. Apart from cellulose and chitin, lignin is one of the aromatic, renewable, and bio-based biopolymers found in abundance in nature [17, 224]. Lignin is a biopolymer that is produced by plants, and it is important to note that lignin makes up 15–36% of the dry weight of wood. It is an aromatic macromolecule with a high functional group density, resulting in an excellent pioneer

for sustainable biomaterials [233, 276]. Among the many sources of renewable and bio-based carbon, lignin is a significant contributor [82]. In terms of concentration in the biosphere, about 30% of the total organic carbon is made up of lignin [32]. This biopolymer has been underutilized until recently, but because it has been shown to provide outstanding characteristics in composite materials and its valorization would be a step forward in sustainability [171, 254]. The development of a simple and effective method for lignin extraction and lignocellulosic biomass processing is important for long-term sustainability [263]. Protic ionic liquids (PILs) have been successfully utilized to extract and recover lignin from lignocellulosic biomass [4]. Dissolution and processing of biopolymers are one of the world's oldest chemical processes, and various major inventions have occurred in this field. Biopolymer extraction commonly employs deep eutectic solvents, ionic liquids, and bio-derived solvents [210]. Biopolymers made from natural resources provide a new, adaptable, and ecologically friendly feedstock that has the potential to have closed-loop life cycles as a component of the industrial ecology of the future. Ionic liquids (ILs), with promising green solvents, recently emerged with a growing respect for their unrivaled biopolymer processing capacity [155].

Ionic liquids (ILs) were explored as aprotic green solvents for the dissolving of lignin separated from the pine-kraft pulp by Pu et al. [211] and observed that [hmim][CF₃SO₃], [mmim][MESO₄], and [bmim][MeSO₄] could dissolve up to 20% of lignin. 2-methyl tetrahydrofuran (2-MTHF) is a good solvent for the extraction of lignin from deep eutectic solvents (DESs) [254]. Tabasso et al. [267] developed a microwave-assisted cascade technique in which GVL (γ -valerolactone) was utilized in an aqueous acidic solution to extract all of the biomass lignin. Achinivu et al. [5] devised a straightforward and exceptionally successful method for extracting lignin by employing a possibly affordable protic ionic liquid (PIL). Wang et al. [284] showed that DESs can be utilized to extract C-lignin from low-cost, abundant castor seed coatings, yielding high-purity C-lignin biopolymer. Lignin, one of the most common polymers in nature, qualifies in the capacity of possible renewable energy source for the synthesis of bio-based aromatic fine chemicals due to its polyphenolic composition [298]. The manufacture of lignin-based biopolymers is the most optimistic technology in terms of lignin valorization and long-term viability. The utilization of lignin increases the possibility for the production of biopolymers such as polyhydroxybutyrates, polyhydroxyalkanoates, and polyurethane, among others [214].

2.1.3 Extraction of Alginate-Based Biopolymers

Alginate, also known as alginic acid or algin, is an anionic polysaccharide isolated from the cell walls of brown algae such as *Macrocystispyrifera*, *Laminariahyperborea*, *Ascophyllum nodosum*, and a variety of bacterial strains [265]. Alginate is a biopolymer that is widely used in a variety of applications. Alginate's hydrogel-forming properties, chemical structure with carboxylate moieties and hydroxyl,

biocompatibility, biodegradability, and water solubility have expanded study opportunities in biomedical sciences [72]. Alginate is a 1,4-linked block copolymer comprising β -D-mannuronic and α -L-guluronic acids [141, 221]. Alginate is a biocompatible anionic polymer with carboxyl end groups that produces stiff hydrogels by easy gelation with divalent cations [26]. Alginate is both inexpensive and harmless [31]. Alginates are natural polysaccharides made up of uronic unit sequences that are derived mostly from brown algae [203]. For the first time in the last century, polysaccharide-based alginate was extracted from marine macroalgae, but after 80 years, *Pseudomonas aeruginosa* was discovered as the bacterial source [77]. Florez-Fernandez et al. [74] used an ultrasound-assisted method to extract alginate from *Sargassum muticum* brown seaweed. A green treatment was used to convert the recovered alginate from the liquors of fucoidan and phlorotannin fractions to alginic acid sodium salt. *Sargassum muticum* is a brown invasive algae that has a detrimental effect on ecological, fishing, and leisure. It has also been linked to changes in biodiversity because it competes with autochthonous algae for light, space, and nutrients [75]. Nadi et al. [179] investigated the inhibitory impact of the brown seaweed *Sargassum muticum* extract (ESM), obtained from Morocco's Atlantic coast, on carbon steel (CS) corrosion in a 1 M HCl medium and discovered that ESM is an effective mixed corrosion inhibitor. The alginate biopolymer is abundant in the methanolic crude extract of *Sargassum muticum* (ESM). Chee et al. [44] used a hot and cold technique to extract alginate from brown seaweeds (*Turbinaria conoides*, *Sargassum baccularia*, *Sargassum siliquosum*, and *Sargassum binderi*) obtained from Port Dickson, Peninsular Malaysia. Yuan et al. [294] designed a process for alginate extraction from brown macroalgae *Ascophyllum nodosum*, by application of microwave technology. Bertagnolli et al. [28] recovered alginate from brown seaweed *Sargassum filipendula* from Brazil and studied the products for chromium biosorption. Janarthanan et al. [108] extracted sodium alginate from brown marine algae *Sargassum wightii* and *Padina tetrastromatica*. Fawzy et al. [70] recovered alginate from *Sargassum latifolium* by using different conditions of alkali treatment.

According to [229] alginate biopolymer (extracted from brown seaweed) resolves the lithium battery LiMn_2O_4 cathode problem. In sorbent-based microextraction, alginate biopolymers are useful [197]. Alginate is a green corrosion inhibitor that is quite effective. Jmiai et al. [113] investigated the anti-corrosion behavior of sodium alginate (SA) on copper in a 1 M HCl medium and observed that the inhibition rises with SA concentration and peaks at 83% at 0.1 mg/L. Faidi et al. [64] used a modified emulsification technique to make clove essential oil-loaded microspheres utilizing sodium alginate derived from a Tunisian brown seaweed Algae *Padina pavonica* as a biopolymer. Antibacterial textile finishing was introduced as a required procedure, and alginate, a sustainable biopolymer, played a key role from the perspectives of environmental friendliness, industrialization, and economic considerations [146]. Alginate biopolymer has been employed in the development of numerous wound dressing products [279].

2.1.4 Extraction of Pectin-Based Biopolymers

Pectin (PECT) is a polysaccharide family that includes galacturonic acid (GalA) linked at α -1,4 locations found in plants cell walls that composes roughly 35% of the principal cell walls of dicot plants and non-graminaceous monocots, as well as 2–10% of grass and 5% of woody tissue walls that allows them to expand as well as extend their cells [73, 170, 286]. This is a plant-derived biopolymer and is separated as a bioplastic material that can be used for a variety of purposes, including food packaging [166]. Pectic polysaccharides such as apiogalacturonan, xylogalacturonan (XGA), homogalacturonan (HG), rhamnogalacturonan I (RGI), and rhamnogalacturonan II (RGII) are present in the plant cell wall and participate in pectin synthesis [16]. Pectin is found in the cell walls of *Arabidopsis thaliana* leaves to the tune of 50% (w/w), however, the number of pectic polysaccharides varies according to species, tissues, and environment in which the plant is growing [91].

The increased demand for pectin has driven the hunt for raw resources including sisal waste, cocoa husks, and peach pomace, *Citrullus lanatus* fruit rinds, orange peels, mango peels, and banana peels for use in the extraction process [159]. It's worth mentioning that conventional pectin extraction takes a lot of time and energy, as well as the usage of mineral acids [205]. Rodsamran et al. [227], examined the Microwave Heating Extraction (ME) of pectin from pineapple peel yielded 1.02–2.12% with excellent pectin quality. The entire pineapple peel pectin extract solution (PPS) was used as a solvent and natural plasticizer in the film production process. Thu [271] recovered Pectin from peels of fruits using the conventional heating process and Microwave-assisted extraction procedure. Garcia-Garcia et al. [79] had also extracted pectin via microwave-assisted technique utilizing waste orange peels. Banana peels are one of nature's most prolific wastes, and their abundance has resulted in the extraction of useful pectin in large quantities. Ultrasound-assisted methods have been shown to extract pectin in research [23]. Another experiment involving pectin extraction from orange peels consisting of acid hydrolysis of the peels followed by filtering of the hydrolyzed suspension, and then alcohol treatment for pectin precipitation [38]. Satari et al. [236] reported that citrus trash was used in a unique pectin extraction method involving dilute nitric acid and ethanol. Citrus trash was transformed into bio-derived compounds using this method. Hot dilute nitric acid was used to extract the pectin, and 95% ethanol was utilized to precipitate the extracted pectin in the solution.

Pectin was identified to be an environmentally friendly inhibitor of acid corrosion in the 6061 aluminum alloy [68]. Rao [289] highlighted the value of biopolymer mix as a corrosion inhibitor and showed its potential to improve epoxy resin coating qualities on steel during acid corrosion. Over the last several years, biopolymers have captivated the interest of both academics and entrepreneurs [253]. As a gelling agent, it is traditionally employed in the manufacture of jams, jellies, and marmalades [205]. There is a lot of space for future growth in the food sector (for stabilizing, thickening, capsular agent, and packaging), biotechnological processes, and medicinal applications, and the most appropriate polymer pectin is employed in these areas [160]. The

use of microwave and ultrasound radiation, as well as enzymatic augmentation of the extraction process and the use of subcritical water to substitute acidified water as a solvent, appear to be the most plausible possibilities for pectin [6]. Xia and Matharu [288] used subcritical water extraction (SWE) in absence of mineral acid to extract pectin from mango peel waste, with the Kesar variety yielding the greatest yield of 18.34%.

2.1.5 Extraction of Xyloglucan-Based Biopolymers

Xyloglucan (XG) is a mucoadhesive and abundant polymer from the hemicelluloses group [76]. Xyloglucans (XGs), often known as amyloids [168]. *Salvia hispanica*, *Hymenaeacourbaril*, *Guibourtiathymenaefolia*, *Detariumsenegalense*, and *Tamarindus indica* all contain xyloglucan [15]. *Tamarindus indica* L. belongs to the Leguminosae and tamarind seeds are a rich source of xyloglucan. In nature, it is biocompatible, biodegradable, and harmless [43, 59]. This biopolymer is a heteropolysaccharide with a 1,4-D-glucose backbone [137] (Fig. 2).

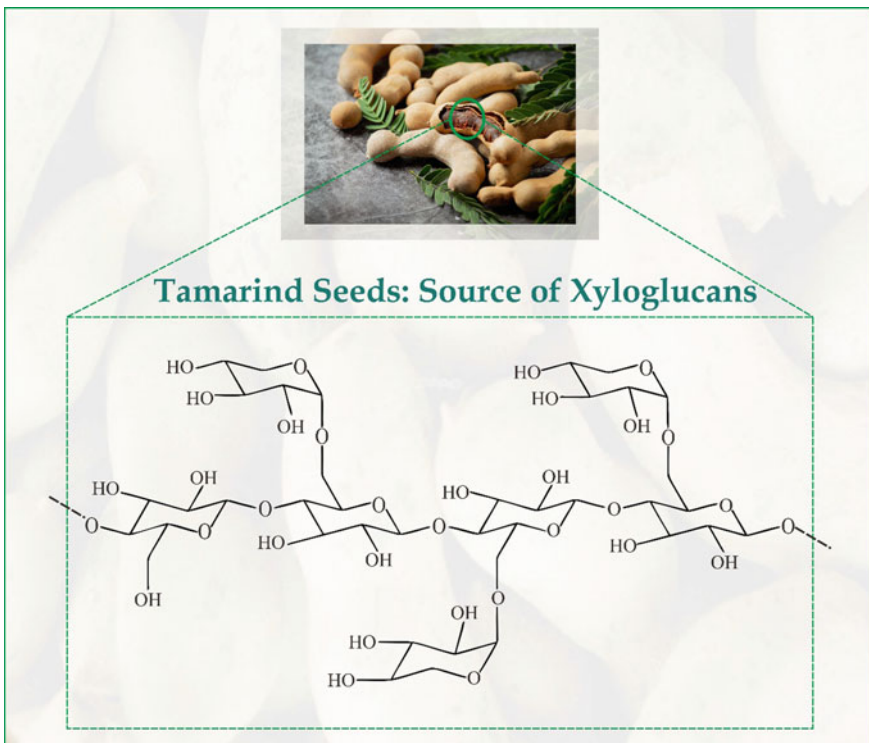


Fig. 2 Structure of Xyloglucans

Various methods for extracting polysaccharides and xyloglucan from tamarind seeds have been documented in the literature [251]. For the first time, [131] investigated xyloglucan (XG) from tamarind seed waste as an alternative high-performance biopolymer derived from the non-food feedstock. Xyloglucan is purified and dissolved in water to make the films. Xyloglucan films offer strong strength, stiffness, and oxygen barrier performance [132]. Microwave treatment was used for tamarind seed decortication followed by xyloglucan extraction by Nguyen et al. [187]. Limsangouan et al. [148] used high-pressure processing to extract tamarind seed xyloglucan from tamarind kernel powder. Nie and Deters [188] extracted xyloglucans from *Tamarindus indica* L. seed using cold water (TSw) and copper complex precipitation (TSc), which were then analyzed in vitro for composition and effects on cell viability, proliferation, cell cycle progression, migration, MAPK phosphorylation, and gene expression in human skin keratinocytes (NHEK and HaCaT) and fibroblasts (NHDF). Lucyszyn et al. [152] extracted Xyloglucan from *Hymenaea-courbaril* (jatoba) seeds. *Detariumsenegalense*Gmelin is an African leguminous plant that has been used as a thickening factor in Nigerian cuisine for centuries. Water-soluble non-starch polysaccharide (s-NSP) xyloglucan is abundant in *Detarium* seed [283]. Rodrigues et al. [226] synthesized Xyloglucans from tamarind kernels and utilized them to make emulsion films with varying sesame seed oil concentrations (SSO).

2.1.6 Extraction of Gelatin-Based Biopolymers

Pomegranate (*Punica granatum* L.) peel powder, mango peels extract (MPE), phycocyanin (PC) recovered from the Saharian cyanobacterium *Arthrospira* sp., mango kernel, and green tea extract, *Centella asiatica* (L.) urban extract, *Crataegus pinnatifida* fruit extract were developed into a gelatin film-forming solution (packing film) to ascertain its physical, mechanical, and antioxidant characteristics [7, 46, 89, 118, 163, 219, 287].

Ibrahim et al. [103] discovered the combination of lignocellulosic fibers from citrus tree pruning wastes (antioxidant-rich and biocompatible) and Extracted Gelatin (EG) as a low-cost bioactive biofilm packaging material that could replace hazardous and non-degradable petrochemical polymers shortly. Kadam et al. [115] studied the Physico-chemical and antioxidant characteristics of gelatin and sodium caseinate films containing *Ascophyllum nodosum* (Brown seaweed) extract at 25 and 50% (w/w of base material) with glycerol. de MoraesCrizel et al. [52] developed biodegradable and antioxidant packaging using waste from gelatin capsule production and components derived from juice blueberry processing waste. In a film composition based on gelatin capsule waste, fiber and ethanolic extract derived from blueberry waste were employed at various weights. Mehta and Kumar [165] constructed gelatin-based ion gel films with Choline salicylate.

Bio-sourced gelatin cross-linked membranes suited for heavy metals extraction in acidic solutions were developed by Kamal et al. [116]. In the vapor phase, three distinct compounds were used to cross-link these membranes: terephthalaldehyde

(TPA), ferulic acid (FA), and glutaraldehyde (GTA). κ -Carrageenan, derived from the red seaweed *Acanthophora spicifera*, has anticorrosive, antimicrobial, and anticancer properties. The sol-gel process was used to make a gelatin- κ carrageenan hybrid composite [178]. The impact on the production, structure, and properties of rabbit skin gelatin by the extracted microwave-assisted method was studied by Liu et al. [150]. When compared to water bath extraction gelatin, MAE gelatin exhibited better gel characteristics and produced gels at a slower pace due to the breakdown of more hydrogen bonds.

2.2 Green Extraction of Biopolymers of Animal Origin

2.2.1 Extraction of Collagen-Based Biopolymers

Collagen is one of the most effective and versatile biopolymers because of its low immunogenicity and biocompatibility [87]. Collagen is the protein in most living creatures, and sea cucumber provides a good source of it (Fig. 3) [237]. This animal protein gives tissues mechanical strength and also encourages cell adhesion and proliferation [259]. Marine creatures have recently been touted as potential collagen suppliers due to their lack of disease transmission. The collagen content of fish biomass and by-catch species is particularly high [48, 192, 290]. Natural bioactive compounds (collagen/gelatin) are abundant in marine sponges [249]. Collagen is produced from fish waste (scales and bones), eggshells, and chicken processing waste [47, 124, 218].

Even though there are up to 27 different forms of collagen, type I collagen is the most common collagen found in connective tissue [84]. Collagen is a plentiful protein-based natural biopolymer with numerous biomedical (pharmaceutical, cosmetics, biomaterials, and regenerative medicine) and non-biomedical (leather and film industries) applications [51, 71, 175]. The disposal of large volumes of raw wastes by the leather industry has caused severe environmental problems. Leather tanning waste can be converted into custom-made collagen biopolymers in a variety of shapes (fibers, gels, films, and sponges) [39]. Hydrolyzed collagen (HC) is a natural biodegradable polymer made primarily of raw collagen that is obtained by fleshing and shaving the hide produced during the tannery process. It is inexpensive and can be turned into modified poly amino acids or Biopols through polymerization, esterification, and sulphation [24].

Wounds are a significant healthcare problem that affects millions of people throughout the world. Diabetes and other lifestyle diseases increase the risk of wound complications [230]. Catalina et al. [40] looked into the wound healing and tissue regeneration biomedical characteristics of a porous bio-collagenic polymer in rats and found that after 7 days, rats had significantly improved wound healing in terms of collagen production and wound filling. For many years, the majority of accessible collagen has been generated from waste from the bovine and porcine industrial industries [48]. A simple and green approach to extracting pepsin soluble collagen-II

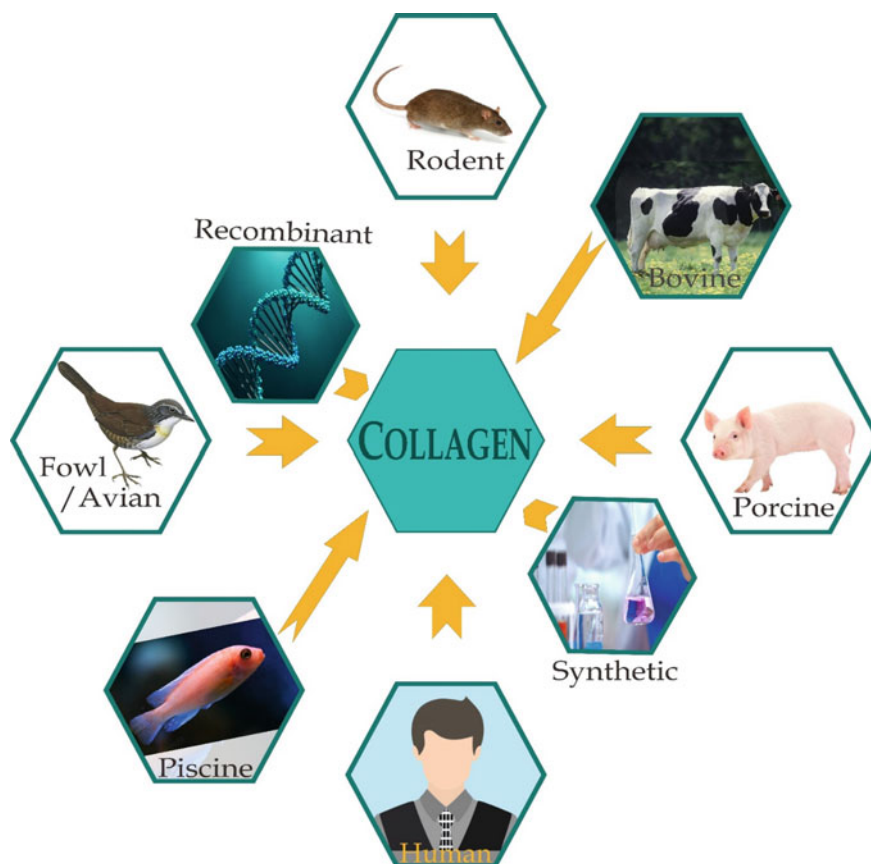


Fig. 3 Major sources of collagen

via ultrasonication was developed by Akram and Zhang [10], which considerably enhanced the extracted yield from chicken sternal cartilage (CSC) and achieved maximum yield in 36 min (UPSCII36, 3.37 g).

Marine biodiversity is exemplified by the diverse variety of vertebrate and invertebrate species found in intertidal to deep-sea environments [67]. Although marine sponge collagen possesses unique physicochemical features, it is difficult to use due to a paucity of supply caused by ineffective extraction methods [20]. Muhammad et al. [175] used a green technique of ionic liquid pretreatment in which ground waste fish scales were processed with $[C_2C_1im][Ac]$ to recover collagen biopolymer. Carvalho et al. [36] obtained Collagen type I from codfish skin and used colorimetric tests, SDS-PAGE, and amino acid content to confirm it. Diogo et al. [58] studied the ability of *Prionace glauca* skin collagen to stimulate the chondrogenic development of human adipose stem cells (hASC) in the presence and absence of an external stimulus. Ben Slimane and Sadok [27] isolated acid solubilized collagen (ASC)

and pepsin solubilized collagen (PSC) from *Mustelus mustelus*. Collagen gels are commonly employed in cell mechanics investigations because they closely resemble the extracellular matrix in physiological settings [114]. Iqbal et al. [104] prepared hydrogels from varied concentrations of collagen up to 60% blended with polyvinyl alcohol.

2.2.2 Extraction of Chitin-Based Biopolymers

Chitin or poly (β -(1 \rightarrow 4)-N-acetyl-d-glucosamine) is the richest renewable polymer generally made from crab shells and mollusks, and it can be deacetylated to become chitosan (Fig. 4) [257, 277, 293]. The second richest polysaccharide in the living world after cellulose is chitin [161, 212, 281, 291]. Braconnot [34] was the first to isolate chitin, a naturally abundant mucopolysaccharide, from the mushroom cell walls, and termed it “fungine.” Odier [191] renamed fungine as chitin 1823 [3, 126]. Chitin is the main component of many fungi’s cell walls and septa [95, 144]. This crystalline polysaccharide is gaining popularity due to its low toxicity, biocompatibility, biodegradability, and biological activity. It has three known polymorphisms (α , β , and γ forms), is hydrophobic, and has a molecular weight of $1\text{--}2 \times 10^5$ Da. In

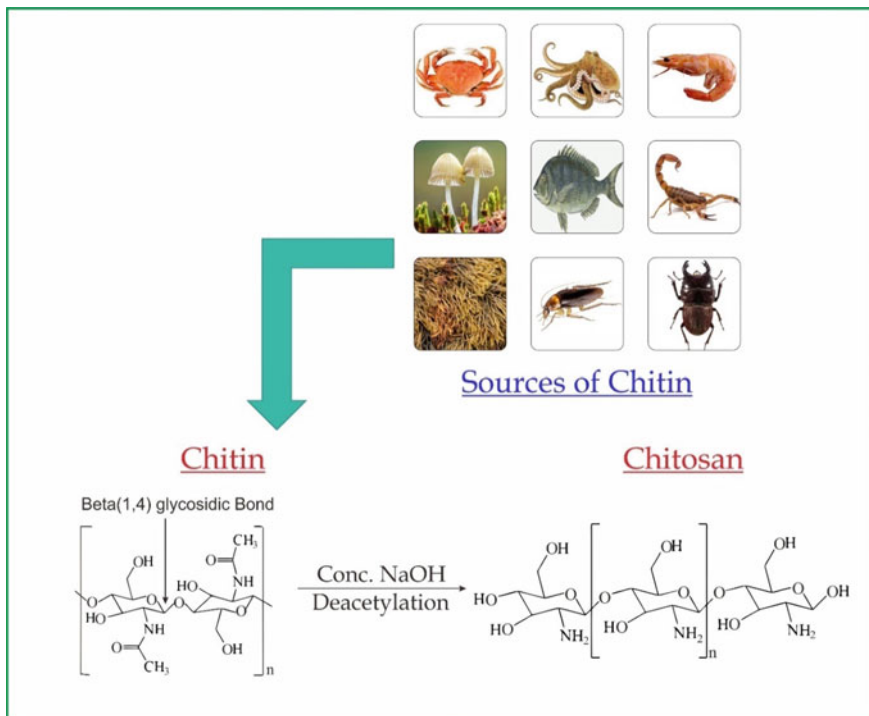


Fig. 4 Chitin Sources and A Schematic Illustration of Chitin Deacetylation

water and most organic solvents, the rigid structure of the chitin biopolymer prevents it from being dissolved [61, 110].

The conventional chitin extraction methods have several drawbacks [204]. There are several options for extracting chitin from diverse sources that have been described. Green technology is actively looking for innovative solvents to replace conventional solvents, which have intrinsic toxicity and volatility, causing volatile organic chemicals to evaporate into the atmosphere [199]. Huang et al. [101] reported an efficient and green approach for extraction of Chitin from Crustacean (Shrimp) Shells using Natural Deep Eutectic Solvents (NADESs), and the extracted chitin was of superior quality with 71% relative crystallinity. Natural deep eutectic solvents (NADESs) are biodegradable, nontoxic, and sustainable solvents that have large melting point depression and become liquids at room temperature. Setoguchi et al. [238] proposed utilizing an ionic liquid 1-allyl-3-methylimidazolium bromide ([AMIM][Br]) to recover chitin from crab shells. The extracted materials were given a DDA value of 7% based on the IR spectra. Ionic Liquids (ILs) based on ammonium [DIPEA][Ac], [DIPEA][P], and [DMBA][Ac] were used to remove chitin from the shells of shrimp.

Chitosan is a natural cationic polysaccharide that has been gaining popularity as a biomaterial in recent years [55]. Chitosan's origins may be traced back to Charles Rouget's work in 1859. Felix HoppeSeyler was the first to coin the term "chitosan" in 1894 [49, 96, 172]. Chitosan has undergone considerable research to reduce the problem of waste disposal [258]. Chitosan was chosen for its unique qualities as a multi-function monomer, for example nontoxic, cost-effectiveness, accessibility, biocompatibility, biodegradability, and ease of polymerization in moderate conditions. The synthesis of a dual template chitosan-based magnetic water-compatible molecularly imprinted biopolymer in water was accomplished utilizing a green process that did not require the use of organic or hazardous reagents [19].

Chemical approaches for extracting CTS from crustacean shells have several drawbacks [122]. Chitosanbiosynthesis has been studied in a large variety of organisms. Sewvandi and Adikary [239] used locally available shrimp type *Penaeus monodon* to create natural biopolymer "chitosan," which involved four major stages: preconditioning, demineralization, deproteinization, and deacetylation. Chitin and chitosan are widely employed in industries, including biomedicine, pharmaceuticals, food, agriculture, and personal care goods, as well as the environment [123].

2.2.3 Extraction of Keratin-Based Biopolymers

Feathers biomass from the poultry industry is a significant waste product that contributes significantly to environmental concerns [246]. These are usually regarded as "waste" that is particularly challenging to dispose of or recycle [117]. Feathers discarded in landfills contribute to environmental contamination and result in the loss of 90% of protein raw material. Keratin is non-combustible, hydrophilic, and biodegradable, which enables it to be used in a variety of ways through chemical processing [215]. Keratin is a significant structural protein that forms the outer coating of the majority of mammals, birds, and reptiles in the form of hairs, wool, feathers,

horns, and nails. It is a biodegradable organic polymer whose biodegradation is facilitated by its strong covalent connections and extensive cross-linking within its structure [11, 140, 245].

Extracting keratins from raw feathers is likewise a difficult procedure [243]. The extraction of keratin was carried out using a variety of procedures, including reduction, oxidation, and processing in ionic liquids [244]. The extracted keratin is analyzed and described using a variety of procedures to validate the presence of proteins and amino acids. The presence of keratin may be determined using the biuret test, and the presence of specific amino acids can be determined using FTIR and XRD analyses [247]. Kumaran et al. [139] extracted keratin from chicken feathers by chemical treatment. The extracted keratin was used to synthesize the hydrogel for wound healing application due to its polymerizing properties.

2.2.4 Extraction of Gelatin-Based Biopolymers

Gelatin is a protein-based biopolymer that is found in the skin and bones of animals [84]. Pig skin, bovine hide, and pork and bones (porcine, bovine, and fish) are the most prevalent sources of gelatin on the planet and can be used to create active packaging with success. Gelatin has different properties depending on where it comes from and what it's used for [190]. Gelatin can be used as a bioactive component and recently found new applications in goods emulsifiers, spray agents, colloid stabilizers, biodegradable film materials and micro-encapsulating agents, pharmaceuticals, particularly in the food sector [62, 125, 260]. Gelatin biodegradable film manufacturing has the potential to assist the industry in decreasing water use, solid waste, power, and emissions [231]. Gelatin has been used to manufacture strong hydrogel-like membranes, microspheres, sponges, and electrospun mats for dermal tissue applications [45, 66, 270, 272].

Gelatin biopolymer is a colorless, practically tasteless protein material produced from collagen through thermal denaturation, is widely employed in a variety of industries because of its technological qualities [180]. Most commercial gelatin comes from mammals, although there is a growing desire for alternate sources for a variety of societal and religious reasons [12, 217, 273]. Fish gelatin (FG) is a protein biopolymer with a regenerative reserve, biodegradability, and processability offers tremendous bio-packaging potential [97]. Antimicrobial and antioxidant agents can be added to biodegradable packaging made from natural biopolymers to create active packaging [105]. Gimenez et al. [83] synthesized a green tea aqueous extract and combined it with commercial fish-skin gelatin at varied ratios (2, 4, and 8%) to generate gelatin films with antioxidant potential.

2.2.5 Extraction of Hyaluronic Acid-Based Biopolymers

Hyaluronic acid, a naturally occurring linear polysaccharide, has captivated researchers since its discovery and separation from tissues. Hyaluronic acid is widely

used in bioengineering and biomedicine because of its biocompatibility and rapid biodegradation [255]. Since its discovery in 1934, hyaluronic acid (HA) has been investigated in a wide range of study areas. This unbranched glycosaminoglycan is extremely universal in humans and other animals. It is composed of repeating disaccharide units of N-acetyl-d-glucosamine and d-glucuronic acid [65]. Almost all animals' extracellular matrix contains hyaluronic acid (HA), which is a substantial component [9].

It has long been recognized that hyaluronic acid (HA) promotes angiogenesis, granulation tissue development, extracellular matrix (ECM) remodeling, and wound healing [102]. It is used to make a variety of wound dressings, including sponges, films, hydrogels, and electrospun membranes [86]. Many tumor cells, particularly tumor starting cells, overexpress hyaluronic acid. They are important in drug delivery systems. Hyaluronic acid is employed in the micelle, polymersome, hydrogel, and inorganic nanoparticle compositions. Many studies demonstrate that HA-based nanomaterials can be used for targeted chemotherapy, gene therapy, immunotherapy, and combination therapy [127].

2.3 Green Extraction of Biopolymers of Microbial Origin

Biopolymers can be synthesized either by biosynthesis (by a living organism, often a microbe) or through chemical synthesis (which suggests synthesis by a nonliving cell). Synthetic biopolymers are described as polymers modified from natural polymers or chemically produced from synthetic monomers in such a manner that they can degrade naturally without leaving hazardous residues for living organisms or natural settings [213]. Polycaprolactone (PCL), polylactic acid (PLA), polyglycolic acid (PGA), polybutylene succinate (PBS), and polyvinyl alcohol (PVA) are examples of synthetic biopolymers that have been developed as a result of technological advancements [109, 135, 223]. There are several advantages to synthetic biopolymers, including developing an environmentally friendly industry, as well as the improvement of several features like durability, crystal clarity, and tensile strength [241].

2.3.1 Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are natural biopolymers and a type of biopolyester made up of 3-hydroxy acid monomers, that are created by fermentation of bacteria and used for energy storage by Eubacteria and Archaea [69, 176, 198, 250]. Bacterial fermentation results in the creation of PHAs biopolymers, which are both biodegradable and biocompatible linear polyesters that occur naturally in nature [21, 193]. PHAs are generated by bacteria, archaea, algae, yeast, plants, and recombinant versions of these organisms [201]. PHAs are still uncommonly utilized because of their high production costs, which are higher than traditional petrochemical plastics

[42]. PHAs are divided into two main categories based on the number of carbon atoms in the monomers: (a) short-chain length PHAs (scl-PHAs) and (b) medium-chain length PHAs (mcl-PHAs). Scl-PHAs are made up of 3–5 carbon atoms and are produced by a variety of bacteria, including *Cupriavidus necator*. *Pseudomonas speciosa* accumulates Mcl-PHAs, which are made up of monomers with 6–14 carbon atoms [136].

PHA is an umbrella word that refers to a group of naturally occurring polymers, the most researched of which is Poly- β -hydroxybutyrate (PHB) [164]. When it comes to extracting PHBs, there are two ways to choose from: chemical digestion surfactant and solvent extraction. Both procedures entail the use of toxic chemicals and result in significant quantitative and qualitative environmental damage as well as economic losses. Biological/bio extraction methods are green approaches and gaining popularity due to their environmentally favorable qualities [88]. PHB generated by microorganisms has the potential to replace non-biodegradable petroleum-based polymers [13]. PHB has a greater production cost than polypropylene [184, 297]. Lemoigne, a French researcher, discovered poly-3-hydroxybutyric acid (P(3HB)) in *Bacillus megaterium* in 1926 [143]. In 300 different bacterial strains, the accumulation of PHAs intracellularly has been examined [22]. It has been reported that Gram-negative and Gram-positive bacteria can produce PHA. *Bacillus*, in particular, has been recognized for its propensity to produce PHA in gram-positive bacteria [169, 250, 252]. Desouky et al. [54] extracted PHAs (69% of the dry weight) from *Bacillus thuringiensis* (KJ206079) using a medium comprising 30 g/L molasses, 0.8 g/L ammonium sulfate at pH 7.5, and an incubation temperature of 35 °C for 72 h. Krueger et al. [138] evaluated 72 bacterial strains for PHA synthesis, finding that *Bacillus megaterium* bioconverts hydrolyzed cassava starchy by-product into P(3HB). Valdez-[278] used low-cost media to extract PHB from fruit peel residues using *Klebsiella pneumoniae* strain E22 (1×10^6 CFU). The strain produced the maximum amount of PHB (23.82 ± 3.39 g/L) after 72 h at room temperature and 150 rpm. Hand et al. [90] investigated the feasibility of employing bacteriophage Ke14 as an efficient extractant to liberate PHB produced by *Pseudomonas oleovorans* cultivated with glycerol containing common biodiesel contaminants. It is possible to generate PHAs in a more cost-effective and long-term way by employing mixed microbial communities (MMCs) [232]. There is a lack of data on the characterization of PHAs recovered from MMCs [193]. Researchers are interested in the algae-based biopolymer because it is one of the alternatives to building a sustainable circular economy across the planet. Microalgae cells contain polyhydroxyalkanoates, which are biopolymers [56]. Polyhydroxyalkanoates are used in a variety of applications including films and containers for packing, disposable carters for chemical and/or medication, disposable goods, surgical pins, stitches/sutures, bandages, bone substitutes, etc. [129, 156].

In addition to having excellent biocompatible and biodegradable properties, poly(3-hydroxybutyrate-co-3-hydroxyvalerate), or PHBV, also has excellent biocompatibility and biodegradability properties, making it a possible option for the replacement of petroleum-derived polymers [225]. It is generated by several different microbes as an intracellular carbon and energy store when they are exposed

to imbalanced growth circumstances such as those found in agricultural feedstock such as sugars and plant oils [149]. PHBV is a member of the polyhydroxybutyrate family with various uses, particularly in the biomedical and pharmaceutical fields. Because of its better physicochemical properties, PHBV degrades at a slower pace than PHB in biological media, making the copolymer a promising long-term drug delivery platform for applications such as encapsulating antineoplastic medicines for cancer therapy [269].

2.3.2 Polylactic Acid (PLA)

In recent years, the most commonly researched synthetic biopolymer has been Polylactic acid (PLA), which is made by condensation polymerization of lactic acid, which may be created by fermentation of carbohydrates [145, 181, 256]. Carothers discovered polylactide (PLA) in 1932, which is also known as polylactic acid. He could only create a PLA with a low molecular weight by heating lactic acid in a vacuum and removing the condensed water from the solution [107]. PLA is classed as an aliphatic polyester because of the ester linkages that connect the monomer units. PLA has grown in popularity in the biomedical area for several applications such as suture threads, bone fixation screws, and drug delivery systems, to mention a few [37]. PLA is a promising biopolymer, and adding nanocellulose to it can improve its characteristics even further. PLA and nanocellulose, which are generated from agricultural resources and agricultural waste, may be utilized to make sustainable, ecologically friendly food packaging [78].

2.3.3 Microbial Cellulose

Bacterial cellulose (BC) is a well-known biopolymer that has recently attracted interest due to its peculiarity characteristics and uses in a wide range of industries. Gopu and Govindan [85] isolated *Komagataeibactersaccharivorans* strain BC1 from grapes and observed that mannitol was shown to be the most effective carbon source, and yeast extract was found to be the most effective nitrogen source. The highest BC dry yield was ~1.81 g/100 mL at pH 5.76 and 30 °C.

2.3.4 Other Biopolymers

Based on polymer source and biodegradability, numerous biopolymers are extracted from the biomass such as Starch, Konjac, Carrageenan, Zein, Gluten, Resilin (Agro-resource; Plant/algae); Pullulan, Scleroglucan, Glucans (Fungal); Xanthan, Curdlan, Dextrans (Bacterial). Furcellaran is a novel natural biopolymer that has the potential to be used in the development of edible films and coatings [158]. The Zein protein is a hydrophobic plant protein that is produced from maize or corn distillers dried grains (DDG) is made of several hydrophobic amino acids and may be used as a food additive

[94, 220]. The magnetic k-carrageenan was produced using an in situ technique and crosslinked through electrostatic attraction with chitosan polysaccharide [154]. In addition, many species produce polymeric materials that require little or no post-processing to extract and utilize the compounds.

3 Assessment of Biopolymer's Sustainability

Plastics have become a vital material in today's world, having a broad spectrum of industrial uses as diverse as autos, packaging, and electrical goods [280] and biopolymers have proven to be viable substitutes for petroleum-based plastics [98]. These are organic polymers derived from biological organisms and consist of monomeric units, which are linked together to form larger formations [41]. The life cycle assessment (LCA) method is a powerful technique for a critical and transparent evaluation of the environment and the effect of material products (Fig. 5) [33, 133]. Gartner and Reinhardt [80] conducted the LCA of several bio-based goods and compared them to conventional products. The environmental impacts of biopolymers can be quantified by LCA. However, biopolymers can be produced into several products for a range of applications and are eventually disposed of in a variety of ways, the environmental implications connected with their creation, usage, and disposal remain unknown [113].

The attributional paradigm has been used in the majority of biopolymer LCA research so far. The attributional approach entails calculating the consequences of a product system without taking into consideration any external factors. Koller et al. [133] developed *SPionExcel* software for LCA of archaeobacterial production of PHA. Ramesh and Vinodh [216] reviewed the LCA of fossil and biopolymers and found that SimaPro software and the Ecoinvent database focused on Global Warming, Acidification Potential, and Eutrophication Potential. Several research used the Cradle to Gate boundary system, with recycling, landfill, incineration, composting, and energy recovery being the most common End of Life (EoL) scenarios. EoL is a crucial step in the environmental implications of plastics throughout their life cycle

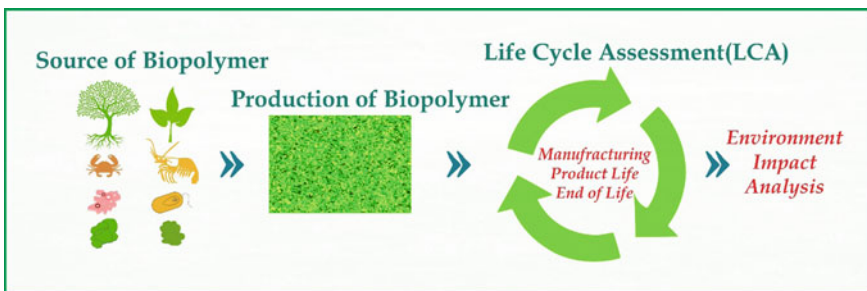


Fig. 5 Life Cycle Assessment (LCA) of biopolymers

[99]. Calderon et al. [35] emphasized the need of using an LCA technique to find more sustainable solutions in the ready-to-eat food industry, such as using packaging technologies. Kookos et al. [134] conducted a complete Life Cycle Inventory and cradle-to-gate LCA of poly(3-hydroxybutyrate) synthesis using soybean oil and, sucrose and revealed clear and unmistakable benefits over petrochemical alternatives. As a result, precise EoL and LCA consequences will be important in future biopolymer sustainability evaluations.

4 Applications of Biopolymers

Biopolymers have a variety of essential uses across a wide range of sectors, including the pharma, biopharmaceutical, food, biomedical, chemical, waste-treatment, and packaging industries, etc. (Fig. 6).

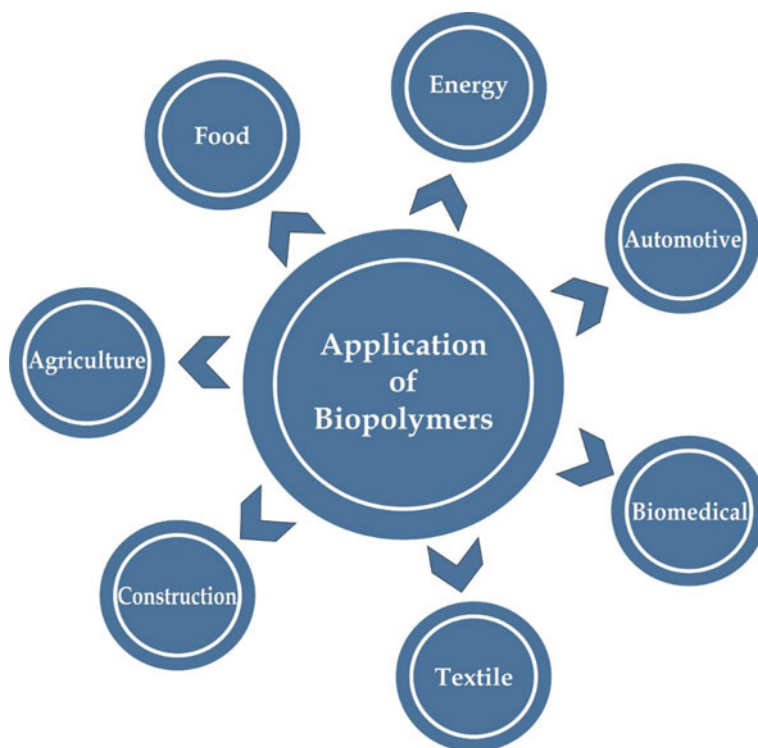


Fig. 6 Applications of Biopolymers

4.1 Biomedical and Pharmaceutical Applications of Biopolymers

In particular, the use of smart biopolymer-based materials made of a range of components to develop innovative solutions in biomedical and pharmaceutical applications appears to be very promising. Ostovan et al. [194] used a Superparamagnetic Molecularly Imprinted Biopolymer (SMIBP) as an ecofriendly bio-sorbent for selective solid-phase extraction and baclofen isolation from urine samples. Bagheri and Ghaedi [19] developed a green, water-compatible, and biocompatible sorbent for the simultaneous preconcentration and determination of valsartan (VAL) and losartan (LOS) in urine samples. Laza et al. [142] developed montmorillonite-ulvan nanocomposites with intercalated and exfoliated nanoparticles which is a water-soluble polysaccharide biopolymer derived from green algae. Madany et al. [153] investigated the extraction of ulvan from *Ulva fasciata*, stressing its usage in biomedical and industrial nanofibrous web manufacturing. Biopolymers have piqued the interest of researchers and industry in recent years, and they've found uses as antioxidants and antimicrobials [253].

4.2 Applications of Biopolymer in Food and Packaging Industries

The effective application of biopolymers and prospective alternate routes resulting from green materials that have a lower carbon footprint augur well for the future development of increasingly complex green materials [261]. High-quality food is in high demand among consumer commodities as well as environmental waste caused by non-biodegradable plastic packaging materials on a petrochemical basis have stimulated interest in the development of biodegradable packaging materials that are produced from annually renewed natural polysaccharide and protein polymers [222]. Pinto et al. [207] synthesized and characterized biopolymer hybrid composites for food packaging. Antimicrobial and antioxidant agents can be added to biodegradable packaging made from natural biopolymers to create active packaging [105]. Chitosan (CS), along with polysaccharides, proteins, and lipids, is one of the most popular components used in the creation of biodegradable packaging [57]. Petroleum-based electronic components pose significant health and environmental problems, and producing conductive biopolymer materials with strong mechanical characteristics remains a challenge. Li et al. [147] developed an environmentally acceptable and sustainable technique for the fabrication of soy protein-based nanocomposite films by combining Cellulose Nanofibril Template-Directed Pyrrole hybrids with a Phytic Acid. Kanmani and Rhim [119] created natural biopolymer-based antimicrobial packaging films to replace synthetic packaging films manufactured with grapefruit seed extract and agar. A novel one-step green water-based method has been devised

to convert vegetable waste into bioplastic sheets with mechanical characteristics like polymers [202].

4.3 Biopolymers in Textile Industries

Biopolymer fibers have been used for textile technology from before the beginning of the recorded history of the human race. Biopolymers are intelligent, environmentally friendly polymers that can be used for several purposes and applications. In the textile industry, a new method to produce bioactive textiles on a broad basis or for the development of next-generation environmentally friendly applications is to employ low-environmental impact technology based on sustainable biopolymers [106, 292]. The use of technology with low-environmental effects gives a fresh path for large-scale development of bioactive and antimicrobial textiles among the possible options begun by the textile industry [128, 174, 240] employed chitosan (a natural biopolymer) as a moderating agent to boost cotton fiber affinity to the green extract polyphenolic components and the chitosan mordant green tea-dry cotton had improved coloring and UV protection compared to unmordant green tea-dyed cotton.

4.4 Biopolymers in Environmental Applications

Heavy metals, organic colors, and oils have all been removed from diverse industrial wastewaters using biopolymers and their derived materials. Biopolymer materials have the potential to provide a long-term sustainable alternative to petroleum-derived products in the wastewater treatment industry. Biopolymers in wastewater treatment as adsorbents and natural flocculants are becoming increasingly popular [200, 299]. Biopolymers produced from algae biomass are employed for environmental remediation, adsorption, and antioxidants. These natural polymers have been demonstrated to be quite successful at removing potentially hazardous components, extracting more than 40 mg PTE/gram of biopolymer [120]. Fadairo et al. [63] studied the extraction and performance evaluation of banana peel-derived polymer and mango kernel-derived polymer for enhanced oil recovery applications. Banana peel waste-derived polymer solution recovered oil between 30.9 and 39.3% while mango kernel-derived polymer solutions exhibited superior recovery between 40.6 and 50.8% of the initial oil in place after waterflood. Ostovan et al. [195] proposed a new green synthesis strategy for preparing multi-template molecularly imprinted biopolymers (mt-MIBP) in aqueous media with less organic solvent consumption. Demand for seafood has increased rapidly, leading to the discarding annually of millions of tonnes. The wastes in chitin, a natural biopolymer, are considerable. Chitosan, a deacetylated version of chitin, has gotten a lot of interest as a heavy metal adsorbent for safe drinking water [25].

4.5 Applications of Biopolymers in Building and Construction Industry

Green composites are materials with environmentally beneficial properties that are technically and economically possible while reducing pollutant generation [1]. Concerns about the environment have prompted the development of green composites to replace non-biodegradable plastics. Torres et al. [275] studied entirely green composite materials for organic fillers reinforced with agroforestry waste. There was a trend in the last decade to use new forms of biopolymers that can be used as wall materials or complete material replacements for maltodextrins and gum arabic [234]. India, as a prosperous nation with limitless resources, provides us with a large range of biopolymers that were utilized in ancient architecture. Many RCC structures were created in the last century, however, they always need to be repaired within 10–20 years of their completion. Biopolymers are employed as corrosion inhibitors, resulting in environmentally beneficial, cost-effective, and long-lasting constructions [29]. Bamboo fibers were investigated as reinforcement fillers for biopolymer composites and nanocomposites by El Foujji et al. [60], owing to their excellent mechanical characteristics. A range of biomass components generated from renewable resources has been developed for use as smart enforcement agents in biodegradable biopolymers, such as coffee (CG), nanocellulose, and date stones [173]. The expansion of sustainable building materials is essential to meet the global demands of a green and sustainable economy. Shanmugavel et al. [242] employed natural additives such as biopolymers to build high-quality sustainable concrete (Cactus extract). The plastics sector is currently undergoing a green revolution, and biopolymers are scarce and expensive, making them an inefficient alternative. Wine waste could be used to make biopolymers such as natural reinforcing fillers, thereby minimizing biopolymer costs [183]. There have been numerous research investigations on the use of semiconductor photocatalysts to reduce anthropogenic aquatic pollutants like organic dyes, insecticides, and cosmetics. Many of these photocatalysts are considered secondary pollutants. Pollution problems can be solved by using green synthesized photocatalysts and biopolymers [264].

4.6 Biopolymers in Electronics, Nanotechnology, and Green Separation Sector

Electronic petroleum components pose a massive public and environmental danger [147]. Flexible electronic devices such as e-skins and strain sensors can be made from natural biopolymers that have been tuned for high-performance flexible electronic devices [285]. Rechargeable batteries are all over, and their use is expected to explode in the coming years [151]. Biopolymers can aid in the development of sustainable and ecofriendly “green battery” systems by acting as long-lasting battery components as Lithium Secondary Batteries (LSBs) [111]. Torabfam and Jafarizadeh-Malmiri [274]

proposed using aqueous chitosan solution and microwave irradiation to make silver nanoparticles (AgNPs) as an economic and ecofriendly alternative to chemical and physical approaches. Agarose is a biopolymer that is utilized as a green separation medium in the form of gels [266]. Different microextraction techniques have been used with agarose and alginate (green biopolymers) [235]. Nanotechnology has the potential to have a substantial influence on a wide range of elements of food systems. Food packaging is being enhanced nowadays as a result of nanoscale technological advancements.

5 Conclusion

This chapter intends to discuss the environmentally friendly extraction of sustainable biopolymers (such as cellulose, chitin, collagen, pectin, xyloglucan, and PHAs, among others) and their versatile applications in the pharmaceutical, construction, food packing industries, automotive, and aerospace, etc. Biopolymers, in particular, have a considerable influence as a potential substitute for petrochemical-based plastics, according to recent developments in biopolymer research. Bio-based polymers are now closer than they have ever been to being a viable alternative to conventional polymers. The selection of appropriate microorganisms using a polyphasic strategy and a cost-effective manufacturing approach are the primary challenges for the economical manufacture of biopolymers. Green methods for the effective extraction of environmentally acceptable biopolymers contribute to the preservation of a safe and healthy environment, which is essential for the achievement of universal sustainable development.

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Abbreviations

NPs	Nanoparticles
LSBs	Lithium Secondary Batteries
PHAs	Polyhydroxyalkanoates
PHB	Poly- β -hydroxybutyrates
PLA	Poly(lactic Acid)
NCC	Nanocrystalline cellulose
MAE	Microwave-Assisted Extraction
ILs	Ionic Liquids
LCA	Life Cycle Assessment
EoL	End of Life
hASC	Human Adipose Stem Cells

CNC	Cellulose Nanocrystals
CNF	Cellulose Nano Fibrils
NADESs	Natural Deep Eutectic Solvents

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Biopolymers from Agriculture Waste and By-Products



Magdalena Mikus and Sabina Galus

Abstract The scale of agricultural waste is large, including crop residues (the plant waste left in the field after harvest), which retained in the field are responsible for agricultural greenhouse gas emissions. Some of those materials are used for organic fertilizer, soil enrichment, or animal feed, but plenty is still available for other uses. The massive amounts of agricultural waste such as stems, leaves, seeds, pods, and more, which never make it off the farm, are a subject of research to use them as bio-based packaging materials. As concerns about waste and by-products grow, researchers around the world are working to turn those materials into useful products and find new ways of using agricultural waste or other unappreciated materials as a valuable biopolymer. The most remarkable works are focusing on the production of bio-based packaging, which can be an alternative to petroleum-based plastics.

Keywords Biopolymer · Agriculture waste · Agriculture by-product · Bioplastics · Bio-based packaging

1 Introduction

One of the most recognized packaging and biomedical materials are materials made of plastics. Today, sustainability and environmental challenges are contributing to the increasingly frequent replacement of petroleum-based packaging with renewable and biodegradable ones [53]. Agricultural waste, by-products, and co-products are usually defined as plants or animal residues that are not (or not further processed into) food or feed, which may even be responsible for additional environmental and economic burdens in the farming and primary processing sectors [43]. Currently, the disposal of waste from the food industry, in addition to reducing environmental pollution, can be a source of added value products. An example of this may be products in which protein is delivered to animal feed [23]. Also, the use of biodegradable cellulose derived from plants, algae, and bacteria can help to reduce production costs,

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improve mechanical properties, and improve the thermal properties of polymers [2]. This represents a growing potential in areas such as bio-nanocomposites, filtration, media packaging, and tissue engineering scaffolds. A by-product of waste biomass from the livestock industry is the remains of bones, feathers, fats, and blood. Huge amounts of such waste generate high disposal costs and generate large amounts of heavy metals, chemicals, and pathogens that can end up in groundwater. One of the interesting applications of keratin, found in animal waste, is its use as an additive to eco-composites and bio-plastic, e.g., in biopolymer films [55]. To further improve resource efficiency and improve agricultural waste management in primary production, it is considered of paramount importance to promote a circular economy approach [3], which is an economical model that produces sustainable goods and services, limiting the consumption and waste of resources (raw materials, water, energy) as well as the production of waste. The goal is to break the linear model (extract, produce, consume, throw away) and replace it with an economical “circular” model [16].

Agricultural waste is mainly a primary residue that can be turned into resources using intensified conversion processes, which may yield potentially sustainable bioproducts such as fertilizers, energy, materials, and molecules. The conversion of this agricultural residue is crucial for supporting the decoupling of economic growth and human well-being from (primary) resource use, preventing putting pressure on land, causing adverse effects on biodiversity, and jeopardizing global food security [62]. Improperly stored or utilized fruit and vegetable waste may pose a microbiological hazard and have a negative impact on the natural environment. The discarded residues of fruit and vegetables are rich in ingredients necessary for a balanced human diet, which, by using appropriate methods, can be recovered from waste and intended for consumption [34]. Among nutritional substances, polyphenols, flavonoids, carotenoids, phytosterols, and anthocyanins can be listed. The main issue that must be taken into account when planning the recovery of valuable components from waste is the profitability and economy of the project [1].

A by-product is an intentional and inevitable material created during the same production process as the main product. According to the Food and Agriculture Organization (FAO), 20–30% of fruit and vegetables become harvest waste. Therefore, taking into account the problem of environmental pollution on a global scale, a significant development of biopolymer plastics is necessary. This will reduce environmental pollution with plastics such as polypropylene (PP) and polyethylene (PET) [37]. It is estimated that approximately 1.3 billion tons of food are wasted in the world every year, which is 1/3 of the food produced in the world. In the coming years, an increase in the received food waste is also expected, due to the acceleration of the global population and economic growth. Expected growth could be as high as 138 million tonnes of food by 2025 [54]. Also in connection with the intensification of livestock production, there are concerns related to the increased emission of methane and ammonia, as well as water, soil, and air pollution [33].

This chapter presents the directions of development of the management of by-products from the food industry, aimed at replacing non-biodegradable plastics with

biodegradable ones. The sources of origin of selected biopolymers and their characteristics, their use in industry are also presented, as well as the future directions of their application development.

2 Biopolymers

Biopolymers are classified as natural polymers produced by plants, animals, and microorganisms, which present biodegradability, which is their main advantage [41]. Currently, biopolymers are also characterized as ethylene-absorbing materials, protecting against UV radiation and reducing microbial contamination of fruits and vegetables. Effective antimicrobial activity has been reported for *Bacillus subtilis*, *Escherichia coli*, and *Listeria monocytogenes*. Moreover, these materials may be a promising component of intelligent packaging systems [37]. Bio-based polymers may be divided into three main categories according to their origin and production:

- Polymers directly extracted/removed from biomass: polysaccharides such as starch and cellulose, and proteins like casein and gluten.
- Polymers produced by classical chemical synthesis using renewable bio-based monomers: Polylacti acid (PLA), a biopolyester polymerized from lactic acid monomers.
- The monomers themselves may be produced via fermentation of carbohydrate feedstock by microorganisms or genetically modified bacteria: polyhydroxyalkanoates.

Various types of biopolymers are known due to the way they are obtained. In connection with the above, a group of polymers of natural origin and a group of polymers of synthetic origin are distinguished. Polymers of natural origin can be divided into three classes: polysaccharides, proteins, and polyesters. Among the polysaccharides, the most famous substances are: cellulose, starch, pectin, chitosan, while among proteins, milk proteins, beans, proteins, corn zein, gelatin, collagen. According to the latest literature, it is possible to differentiate between three types of biopolymers:

- Biopolymers that are made from renewable raw materials (bio-based) and are biodegradable.
- Biopolymers that are made from renewable raw materials (bio-based) and are not biodegradable.
- Biopolymers that are made from fossil fuels and are biodegradable.

Cellulose, defined as the polysaccharide that is most abundant on earth, is a natural polymer of hydroglucose. Increasingly, cellulose fibers are used instead of glass fibers because of the desired properties. They include, among others, biodegradability and an appropriate shape factor. Recently, there has been an increased interest in cellulose acetate (CA), which, in addition to being a biodegradable polymer, enables excellent optical clarity and material strength to be obtained [59].

Casein, which makes up 80% of cow's milk protein, is in the form of a suspension of particles. It has found applications in many industries, such as the food industry, plastics, and medical products. Casein, being a waste of dairy products, can be used to improve and fertilize the soil, thus allowing for effective waste management. Casein recycling can also significantly reduce greenhouse gas emissions [12].

Gluten, a vegetable protein found, among others, in cereals such as rye, wheat, and barley, it is a by-product of bioethanol production and is mainly used in the production of animal feed. Gluten has also been used in the production of bioplastics and due to its ability to cross-link, it can increase the viscoelastic properties of the material, which is related to the strictly defined extrusion conditions. Pressure, temperature, operating time, and mechanical energy have the greatest influence. The wheat gluten used to form plastics is a suitable material for the formation of forming films used in food packaging. However, it should be remembered that 1% of the world's population suffers from celiac disease, and in Europe, this percentage accounts for 0.3–2.4% of the population, which limits the use of gluten-based bioplastics on an industrial scale [27].

One of the most attractive biodegradable materials is polylactic acid (PLA), which has excellent transparency and relatively good water resistance compared to proteins and polysaccharides. For this reason, polylactic acid is of great interest in food packaging, also having similar properties to conventional plastics such as PET and nylon [27]. PLA, as a biodegradable material with high development potential, is obtained by fermenting carbohydrates with *Lactobacillus*. Research on PLA products has also been carried out using renewable agricultural resources such as sugar beet. Polylactic acid has good mechanical and thermal properties but has an average water and oxygen permeability that is comparable to polystyrene. Due to its low heat resistance and tendency to crumble, its use is limited. PLA is most often used in the production of foil, thermoformed containers and bottles [59].

Pectins, the best source of which are citrus and apple fruits, apart from their ability to bind ions, are also characterized by gelling, thickening, and stabilizing properties. Therefore, they are used in industry as hydrocolloids [14]. Thermal, chemical, or enzymatic modified citrus pectin is registered in the United States as a dietary supplement. Clinical trials have confirmed the antitumor potential of modified pectin, which prevents tumor progression and inhibits metastasis. Citrus pectin also affects the cells of the immune system to regulate the inflammatory response [7].

In industry, starch is commonly obtained from tubers and cereals. An alternative to these raw materials may be the pomace of some fruits, which are characterized by a high content of this polysaccharide. In addition, the starch obtained from pomace has other functional properties, which increases the range of its applications in industry. Kringel et al. [32] pointed to the possibility of obtaining starch, among others, from pineapple pomace, apple, mango, lychee, avocado, or leaf tree fruit. The seeds of the latter are the best source of the discussed polysaccharide, the content of which is 60–80%. The starch obtained from mango pomace has unique properties, because it has a low glycemic index, thanks to which it is used in products with reduced caloric value.

Polyhydroxyalkanoates (PHAs) are polymers produced by PPBS, i.e., purple phototrophic bacteria, which are probably the most metabolically diverse organisms in nature. PPB is characterized, among others, by the ability to develop in anaerobic conditions, which enables a large recovery of carbon from waste materials, such as municipal, agricultural, and domestic sewage. The main bioproducts obtained from PPB are hydrogen, proteins, fertilizers, and other value-added products, however, the use of polyhydroxyalkanoates on an industrial scale is limited due to production costs [21]. One of the observed strategies to reduce the resulting material costs while maintaining biodegradability is combining PHA with cheaper lignocellulosic fibers, which are a by-product of the agri-food industry [8, 9]. Currently, one of the main sources of energy for the production of PHA is glucose obtained from food and vegetable oils. Carvalho et al. [10] tested PHA production from sugar molasses waste, while [26] used olive oil mill wastewater for production. Vega-Castro et al. [63] for the production of polyhydroxyalkanoates (PHA) as a carbon source, they used a cassava peel hydrolyzate derived from agro-industrial residues. Previously, research has been carried out on the production of PHA from cassava starch using strains such as *Cupriavidus sp.*, *Bacillus tequilensis*, and various species of *Bacillus*, or from cassava powder in the presence of *Bacillus sphaericus* strains.

2.1 Sources of Biopolymers

There are many ways that can be used, including extraction from natural sources, by biosynthesis of living organisms, or by chemical synthesis from biological materials, to obtain the bio-based materials. The most commonly used biopolymers forming biodegradable packaging include polysaccharides, proteins, and lipids. Biopolymers derived from animal waste such as inedible tissues and parts of animals are, e.g., gelatin, which is a good source of protein. Among the plant-derived proteins, mention may be made of the soy protein isolate having the ability to retain water and oil, as well as gelling and emulsifying. Lipid polymers are used for their hydrophobic nature and high water barrier properties in food packaging or 3D printing materials. Polysaccharide-based polymers are the most stable and do not undergo irreversible denaturation, while their disadvantages include low mechanical resistance and high sensitivity to water. Pectin, the main polysaccharide, has become increasingly important in recent years and is used, among others, in thickening, gelling agent, and emulsifiers [7]. Other uses of pectin include the coating of fresh fruit and vegetables, and as a nanomaterial used for the controlled release of active ingredients. In addition, as a source of pectin, waste biomass is mentioned, which is by-product of the production of juices and the peel of fruit such as bananas, mangoes, oranges, or pomegranates [38].

Biopolymers are characterized by the ability to form coherent protective layers on the surface of food, known as films and coatings. In addition, the use of natural polymers in food packaging allows you to maintain the quality of products and affects the extension of the shelf life and shelf life of food products. Biopolymers

can also be carriers of antimicrobial substances, vitamins, antioxidants, dyes, and flavors. In this way, it is possible to improve the sensory properties and the nutritional value of the packaged product. Many studies have focused on the introduction of probiotic microorganisms and nanoparticles, e.g., silver, into edible packaging. The content of silver nanoparticles makes it possible to obtain functional nanocomposite materials, such as, for example, improvement of protection against the growth of microorganisms and enhancement of antimicrobial properties in various types of food. The limitations in the use of biopolymer materials are primarily related to poor mechanical properties and moisture resistance [31].

Another source of biopolymer production is algae, characterized by the ability to remove toxic elements, even in the amount of 40 mg PET/g of polymer. Algae with the ability to accumulate carbohydrates, polysaccharides, proteins, oils, polymers, and other bioproducts are suitable materials for the production of food packaging. The resulting algae-based composites are biodegradable, with appropriate mechanical and tensile-resistant properties. In addition, due to their high nutritional value, they are a potential food ingredient and have strong antimicrobial, antioxidant, and anticancer properties [29].

Commercially available biopolymers are polylactide (PLA), polyhydroxyalkanoates (PHA/PHB), polyols, polyamides, bio-PET, butyl rubber, and cellulose acetate, and the world's leading producers in the production of biopolymers derived from fruits and vegetables are China and India. Biopolymers obtained from the fruit peel improve the mechanical strength of the polymers produced. Patil et al. [45] conducted a study on powdered lemon and lime peel for this purpose. The improvement of mechanical properties depended mainly on cellulose, lignin, and raw fibers in the fruit peel, which constitute 90% of the fruit. The problem, however, is the availability of this waste, since the scrap fruit peels are used in the production of value-added products, e.g., as bioactive polyphenols with antioxidant properties (Fig. 1).

2.2 *Agriculture Waste*

Population growth and nutritional changes are factors that contribute to higher consumption of fruit and vegetables, which results in an increase in their processing waste [32]. In Europe, fruit processing by-products account for 8% of all food waste. This industry is the fifth largest producer of waste. The situation is much worse in developing countries, where the by-products of fruit processing are treated as irrelevant and redundant compared to processed fruit [42]. A global food waste amount is large, approximately 1.3 billion tons per year. In addition, the food industry is responsible for a large amount of fruit and vegetable waste, which are the biggest losses and are estimated at half a billion tons per year. The waste is a result of the processing of vegetables and fruit, including peeling and juicing. A side effect of juice production is large amounts of waste, which account for between 30 and 40% of the waste of the entire agri-food industry. Fruit and vegetable waste resulting from

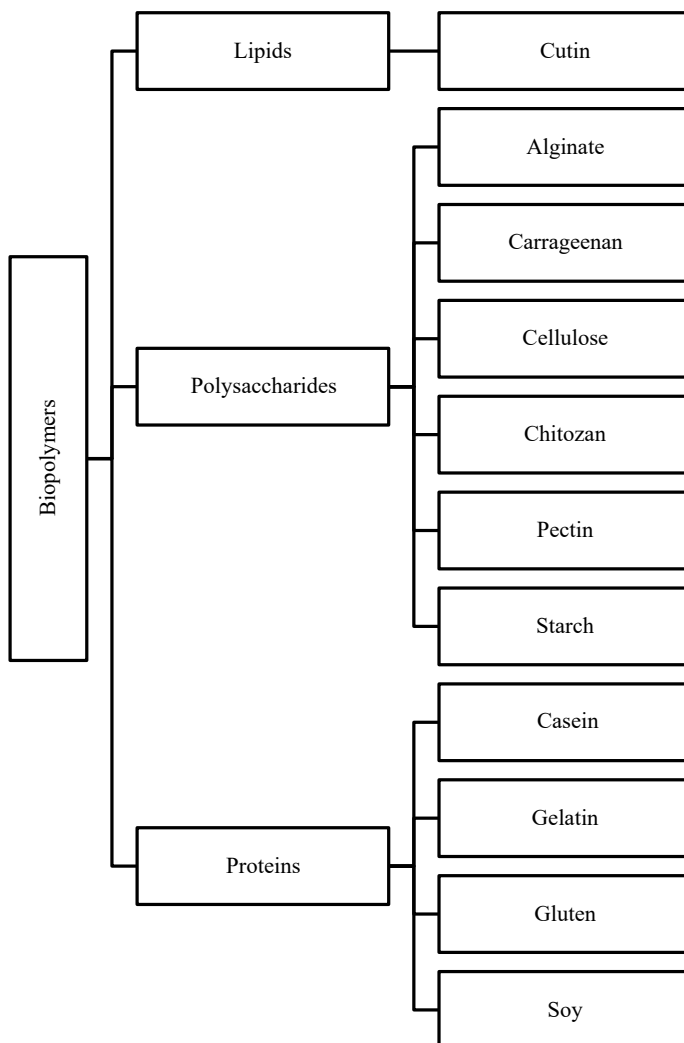


Fig. 1 Different types of biopolymers

the production and processing of the food sector include: skin, seeds, stems, bagasse, scales, leaves, grains, and much more [4]. In fruit and vegetable processing, a significant problem is the management or utilization of waste products—parts not used in the technological process. Their amount is in the range of 10–35% of the weight of the processed raw material. Currently, the most popular way of using pomace is to use it as feed, which allows for a significant reduction in the cost of animal feeding. In addition, they contain important ingredients such as: organic acids, sugars, fatty substances, nitrogen-free compounds, and vitamins which content in the pomace

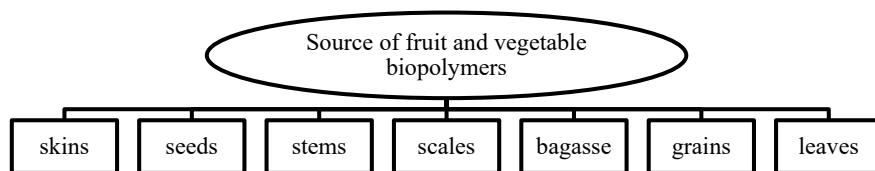


Fig. 2 Source of fruit and vegetable biopolymers

after juice pressing process, depending on the conditions of the process, may be as high as 2 g/kg of dry matter [60] (Fig. 2).

Improperly stored or utilized fruit and vegetable waste may pose a microbiological hazard and have a negative impact on the natural environment. The discarded fragments and residues of fruit and vegetables are rich in ingredients necessary for a balanced human diet, which, thanks to appropriate methods, can be recovered from waste and intended for consumption. Among them can be mentioned polyphenols, flavonoids, carotenoids, phytosterols, and anthocyanins. The main issue that must be taken into account when planning the recovery of valuable components from waste is the profitability and costs [1].

Consumer demands for products are increasing. Sometimes the manufactured product does not meet the quality classification requirements related to appearance, shape, size, or texture. Despite its suitability for consumption, the product is not intended for sale. In the case of the vegetable industry, such waste is called vegetable out grade. During processing, it may happen that some fruit or vegetables, such as cauliflower or broccoli florets, are considered too small and do not meet the classification requirements. On the other hand, it is still a full-fledged vegetable. In this case, broccoli florets can be used, for example, in the production of many preserves, including vegetable burgers or vegetable spreads [46].

The fruit and vegetable pomace is a material characterized by low durability and stability. Fruit pomace, due to the high water content, which is up to 73% in apple fruit, is exposed to a rapid increase in microbiological contamination. The most popular methods of preserving pomace include drying and ensiling, which inhibit unfavorable changes leading to a reduction in quality. Using different treatments caused that pomace is suitable for further use [60]. Due to the content of many health-promoting ingredients, in recent years, there has been a noticeable increase in interest in the possibility of reusing processing fruit and vegetable pomace which is rich in pectin, fibers, and phytochemicals. In the case of apples, most of the polyphenols remain in the pomace during pressing and only 5% of it passes into the pressed juice. The pomace contains a high water content, which poses a microbiological risk during the storage of this waste. To reduce the above risk and extend the shelf life of the pomace, a drying process was used [44]. Moreover, pomace is a source of many other valuable nutrients, such as: minerals, saccharides, proteins, organic acids, lipids, vitamins, aldehydes, and alcohols. They are also rich in aromatics and dyes, including anthocyanins that can give color from yellow to blue. The pomace is characterized by a high content of coloring compounds from berries. This makes it possible to extract

these compounds from the pomace and production of dyes. Phenolic compounds, apart from giving color, show strong health-promoting properties. Along with tocopherols, they belong to the antioxidants responsible for protecting against the harmful effects of free radicals and, as a consequence, it enables the prevention of heart disease, cataracts, and cancer and inhibits the aging process [60].

The current production of plastics is around 400 million tonnes of waste generated each year. Scientists predict that their number will increase four times by 2050. Accompanying growth will be the increased production of agricultural plastics such as mulching materials and pesticide containers. These materials can be hazardous when recycled because toxic and synthetic chemicals may leak. Recycling of artificial waste in the world is only 9% [37].

2.3 Agriculture By-Product

Agricultural by-products represent a large proportion of the untapped biomass resource, which can lead to a significant economic and environmental burden. The management of agricultural waste is a difficult challenge due to the seasonality, regionality, variety, and complexity of crops [57]. According to FAO, the projected increase in the world's population to 9 billion in 2050 will result in increased food production, and thus a proportional increase in agricultural waste. For this reason, an emerging trend based on the circular economy has been observed in recent years. It is also of key importance for the growing world population to implement measures to reduce soil erosion and degradation caused by the intensification of production. For this purpose, the aim is to replace petrochemical polymers with biopolymers obtained from agricultural residues [18].

Agricultural by-products are mainly primary residues from which it is possible to obtain bioproducts such as fertilizers and energy. The current challenges related to the management of agricultural waste include, *inter alia* [24]:

- Converting agricultural waste into biogas.
- The use of anaerobic digestate as a renewable fertilizer, which is associated with hygienic and environmental risks, as well as its storage.
- Development of innovative molecules and materials derived from agricultural residues.
- Development of biorefinery methods and innovative cascade technologies appropriately adapted to agricultural waste.

It is worth noting that vegetable waste from agriculture is a rich source of lipids, polysaccharides, which can be used in the production of polymeric materials. Some of the agricultural by-products can also be a source of aromatic compounds (e.g., lignin derivatives), which are used interchangeably with traditional polyesters (polyethylene) [39, 47]. In addition, the beneficial impact of developing bioproducts from agro-waste on reducing EU greenhouse gas emissions to 55% is estimated [17].

Table 1 The example of using agriculture by-products in the preparation of bioplastics

Source of the by-product	Formulation	Properties	References
Rapeseed by-products (e.g., rapeseed cake and meal)	Rapeseed proteins could be also considered as ingredient in the development of bioplastics	Techno-functional properties (e.g., emulsifying, foaming, and gelation properties)	[15]
Agro-industrial waste for lactic acid (cassava bagasse, sugarcane bagasse, corn cob)	–	Lactic acid production	[11]
Fibrous matter of cassava bagasse	Substrates for lactic acid	Economical replacement of expensive refined sugar with starchy materials	[11]
Chitosan	Coated on the surface of PET or polyethylene (PE) catheter	Anti-adhesive and antibacterial abilities	[35]

Whey protein constitutes 20% of all milk proteins and contains a mixture of β -lactoglobulin, α -lactalbumin, bovine serum albumin, and immunoglobulin [50]. Whey is a by-product obtained during production in the dairy industry, and an alternative way of its management is to obtain whey in a powdered form, which is a substitute for powdered milk. It should be noted that large amounts of energy are consumed in the production of whey. To prevent this, the fermentation time should be shortened. This is possible by using the right type of high-performance mixers and applying rigorous in-process control. An important aspect is also the evaporation of the water in the dairy, thus achieving a smaller amount for transport. According to the research carried out, it was found that the production of valuable PHA biopolymers is the process of the processing of whey. Thanks to this, it will be possible to achieve ecological potential, significantly exceeding fossil polymers [30] (Table 1).

3 Applications of Biopolymers in Food Industry

The main direction of waste management in the fruit and vegetable industry is the recovery of valuable ingredients. Potato skins after proper treatment, they become a source of fiber, necessary for the proper functioning of the human digestive system. Polyphenols, including flavonoids, being a bioactive ingredient, are recovered from the peels of citrus apples and grapes, which often become waste after obtaining the juice from the above-mentioned fruits. Lycopene can also be recovered from the waste obtained during the juicing of tomatoes and β -carotene. Pectin is obtained from apple pomace and orange peel, which can be used to make edible coatings and films. Banana peels, which make up about 35% of the fruit's weight, are used, among others, for the production of wine. In addition, it has been observed that the

ingredients present in the pomegranate peel have bactericidal properties, including for *Bacillus cereus* and *Staphylococcus aureus*. Pineapple peel can produce ethanol, and properly processed tomato waste can be used as a substitute for wheat flour. From citrus peels, a syrup is obtained, which is a substitute for sweeteners [1]. Waste from the fruit and vegetable industry can also be used to obtain enzymes. For example, the peel of banana can be used for the production of α -amylase, while strawberry pulp was used as a substrate for the production of polygalacturonase, which is used for clarifying wines and juices, as well as in the production of jams [58]. The high content of fiber also helps to counteract obesity, diabetes, heart disease, atherosclerosis, and some types of cancer [60].

Pomace is also a rich source of biopolymers, proteins, and carbohydrates that can be recovered, concentrated, transformed into precursors, and then used in the cosmetics, pharmaceutical, and food industries. Researchers have made attempts to obtain enzymes, oligosaccharides, biosurfactants, lactic acid, and furfural from the tropical fruit pomace [42]. The pomace can also be used for the growth of microorganisms, which allows to obtain pectinolytic enzymes from pineapple, orange or lemon pomace, mango, or banana amylase or lemon peel lipase. Pomace is an alternative carbon source for glucose and sucrose commonly used in cultivation. This allows for a significant reduction in production costs and obtaining polysaccharides valuable in the industry, such as xanthan gum, pullulan, or curdlan. Mohsin [40] synthesized kurdlan using orange pomace, which, thanks to its gelling properties, is widely used in various industries. The polysaccharide, belonging to β -glucans, is a component of biodegradable films, functional products, e.g., yogurts, and can also be a fat substitute in meat products, reducing their calorific value. Kurdlan is also characterized by immunostimulatory properties, which increases the interest in this compound in medicine.

Waste from the fruit industry can be successfully used in some confectionery and bakery products. Maner et al. [36] replaced a part of wheat flour in cookies with dried grape pomace. From the test results, just like in the previous ones, it was possible to conclude that the addition of bagasse allowed to enrich the products with health-promoting substances while maintaining or imparting appropriate sensory features. Salehia and Aghajanzadeh [51] also described the effect of dried and powdered fruit and vegetables on the quality of the dough. The presence of the powder increased the water absorption, as a result, the dough had a higher moisture content. The reduction in gluten contributed to a reduction in volume and improved firmness. The addition of the powder allowed to increase the nutritional value. The biscuit dough, in which part of the wheat flour was replaced with the powdered skin, and powdered mango pulp contained more fiber, less fat, and calories. Additionally, the dough was enriched with nutritious polyphenols and carotenoids. Fruit pomace is used in the production of gluten-free bread. Enrichment of the recipe of rice flour bread and potato starch in orange pomace made it possible to obtain the product with sensory properties similar to the control sample [49].

Alcoholic fermentation, in which the carbon source is the pomace, also allows for the production of biofuels. The most efficient substrate is apple pomace, which allows to obtain 190 g of ethanol from 1 kg of waste [19]. Piwowarek et al. [48] used apple

pomace as a microbiological substrate in the propionic-acetic fermentation process. The use of apple pomace as a carbon source allowed the cultivation of the wild strain of *Propionibacterium freudenreichii* T82 and obtained acetic and propionic acid.

Apple peels are characterized by a high content of phenols, which means a greater concentration of these bioactive compounds in the pomace than in the whole fruit. Phenolic compounds have strong antimicrobial and anti-inflammatory and antioxidant properties, which can be used for cosmetic preparations, where fruit seeds, rich in valuable oils, have also been used [6]. Commonly used in this industry is raspberry seed oil, which is appreciated for its content of minerals, provitamin A, vitamins B₂, C, and organic acids, including salicylic acid and apple. Due to the chemical composition of the discussed oil, it can be a component of sunscreen preparations, creams, or toothpastes [28].

4 Bioplastics

The term “bioplastic” refers to two types of materials; on the one hand, bio-based plastic materials (made from vegetal resources) and, on the other hand, biodegradable plastic materials, including compostable ones. Unfortunately, at present, the costs incurred in the production of bioplastics are much higher compared to petroleum-based plastics. According to [61], the industrial production of PHA is 5–10 times higher than that of petroleum polymers. To reduce the production costs of bioplastics, there is an increasing tendency to use waste and by-products that will constitute the input material. Bioplastics being a group of materials with various properties and applications can also be classified as edible, considered safe for human consumption, and inedible.

According to data from 2020, the global production of bioplastics amounted to 2.11 million tonnes per year, while in 2019 biodegradable plastics such as PLA, PHA, and starch mixtures accounted for more than half of all bioplastics produced. Nowadays, bioplastics can be distinguished from almost any conventional plastic, which has a positive effect on more environmentally friendly waste management, with the added value of reducing the carbon footprint. Biomass, carbon dioxide, and water are obtained from biodegradable materials that are degraded in aerobic conditions, while in anaerobic conditions, methane is also obtained during the degradation process [27].

Bioplastics are not only plastic bags any more in retail chains and bags for waste but also advanced packaging materials, construction elements for cars, computers, or phones. Biodegradable materials are used in medicine, pharmacy, agriculture, electrical industry, and many others. Therefore, as a sector in a current development, applications of few materials, including those from waste or processing residues are expected. Environmentally friendly materials can be subjected to the same processing, as well as classical material artificial, therefore they are not more difficult in processing and do not require a specific machine park. Biomaterials increase the

competitiveness of enterprises on the market as innovative entities, focused on development and increasing your potential. Therefore, far the main barrier to commercialization and wide application of bioplastics is their price, but due to increasing environmental awareness, many countries need bioplastics increase and they are an opportunity to reduce waste generation and progressive environment pollution.

Currently, bioplastics are only 1% of the global annual production of plastics. The sources used for the production of bioplastics are plant raw materials, natural polymers such as carbohydrates, and proteins. Other small molecules are: sugar, disaccharides, fats, and acids [13]. Packaging made of bioplastics for food based on renewable sources can be obtained in whole or in part from biomass from various sources of plant or animal origin. Starch-based bioplastics are environmentally friendly and with relatively low-cost biodegradable polymers. However, they are characterized by high water vapor permeability, therefore, research is focused on modifying starch films in terms of their functional properties, e.g., by combining with other polymers [22]. The advantage of starch films is a good barrier to oxygen and carbon dioxide. The hydrophilic nature of the polysaccharide can be reduced by chemical, physical, or enzymatic modifications. Modified thermoplastic starch is one of the basic materials for creating biodegradable packaging.

Samer et al. [52] used potato peelings to produce bioplastics. Researchers used the process of extracting starch from the potato skin and adding water, glycerin, vinegar, and industrial dyes. As a result of the subsequent heating process, many variants of bioplastics samples were obtained, which were characterized by different functional properties. Based on the research, it was found that with the increase in glycerin content, the bioplastic becomes increasingly elastic, while with the decrease in glycerin content, it hardens. In addition, it has been observed that when using less starch, more energy is required, which is needed to evaporate more water and obtain stability.

5 Future Trends

The highly popular renewable polymers represent great potential in the food field. The promising results regarding the use of food hydrocolloids and biopolyesters in food packaging structures are of increasing interest to researchers. The use of nanotechnology as well as food encapsulation has brought impressive results in recent years. A dynamically developing area is also the introduction of active and intelligent food packaging techniques, enabling the reduction of the use of artificial packaging. There has also been significant progress in improving the processing of waste from the agri-food industry that can be reused during the production of bioplastics [27]. However, the implementation of technology to transform waste into biopolymers will require the cooperation of sectors at different stages of production. The occurrence of noncompliance and mismatch problems in the production, collection, or distribution of final products is also expected. Therefore, further research should focus on the

Table 2 The example of using agriculture by-products in the preparation of protective edible coatings

Source of the by-product	Application	Advantage	References
Banana peel	Fruits and vegetables	Reduce costs and the environmental impact generated by discarded agro-food waste	[20]
Flour from the remains of fruits and vegetables	Fruits and vegetables	Homogeneity and flexibility without the addition of a plasticizer	[5]
Waste from wine production	Fruits and vegetables	High content of nutrients	[25]
Apple peel	Meat	Maintaining the appropriate quality	[56]
Tilapia Skin Collagen	–	More smooth, uniform, and dense surface for composite films	[65]

capitalization of knowledge and information that will allow the improvement and maximization of reuse of residual waste [64].

Moreover showing promising potential are nanocomposites, which consist of a polymer matrix containing nanoscale particles (nanoparticles). The presence of nanoparticles positively improves the properties of materials and is a promising way to create biopolymers with the desired properties. The conducted research indicates that the addition of nanoparticles may lead to an improvement in the performance of the polymer [31].

The use of refinery waste, which is a source of glycerol and lingocellulosic sugars, ensures the sustainable production of PHA and is a new direction limiting the production of increased amounts of bioethanol and biodiesel. The delays in the attempts to produce bioplastics resulted from high production costs, environmental pollution, and improper use of chemicals. In the future, the ecological and inexpensive production of bioplastics will have to be assessed throughout the development of the business, as this will help to reduce the occurrence of hazards in production. It will also be required to adopt the appropriate methodology for progressive production and to maintain a balance between adequate maintenance of water quality, soil quality, biodiversity, and biomass availability [64] (Table 2).

6 Conclusions

The introduction of industrial agri-food waste in the production of biodegradable packaging materials may replace non-biodegradable plastics in the future. This would significantly reduce the amount of waste generated, as well as reduce production costs. However, due to the relatively poor mechanical and barrier properties of

bioplastics materials, their common use is currently limited. For this purpose, the aim is to modify biopolymers, mix various biodegradable materials, and obtain new ones. A promising method is also to improve the properties of bio-nanocomposites, which will be more environmentally friendly and cost-effective in relation to synthetic polymers. Further research will enable a better understanding of the modifications and structures of bioplastics obtained from agro-food industry waste with improved properties. To reduce the harmful effects of plastic materials on the environment, research is increasingly focused on creating biodegradable packaging as an alternative to crude oil. In this way, it will be possible to solve problems related to problematic waste disposal in the future increasingly advantageously.

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Biopolymers from Industrial Waste



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Abstract The problems arising due to anthropogenic activities and limited availability of resources demand sustainable and smart solution. Uncontrolled waste generation and usage of traditional non-biodegradable materials is one such critical issue. To address the waste disposal problem and to meet the need for bio-based materials, the valorization of leftover biomass residues arises as a green and sustainable approach. Technological advancements have paved the way to use biochemicals and biomass for the formation of biomaterials such as biopolymers. With this viewpoint, the chapter focuses on biopolymers-biodegradable, low cost, abundant, biocompatible, naturally occurring and microbially synthesized molecules. They comprise a wide variety of molecules like cellulose, chitin, collagen, polylactic acid and polyhydroxyalkanoates. The waste material generated from various sectors including food industries, agricultural sector, dairy industry, leather tanning processes and domestic waste is considered as a potential substrate for biopolymer synthesis. Being low cost and renewable raw material, waste biomass is extensively used for the generation of all types of biopolymers. The excellent properties of bio-based polymers make them usable in almost all areas of our daily lives. Biopolymers are widely used in medicines for tissue engineering, regenerative medicines, drug delivery and bone implants. They also possess applications in the food industry as food packaging materials and food coatings. This chapter intends to discuss the formation of various types of biopolymers from waste feedstock and their applications.

Keywords Biodegradable · Biopolymers · Biocompatible · Waste · Valorization

1 Introduction

The environment is being overwhelmed by the usage of non-biodegradable materials for energy and other products. The ever-increasing demand for products and energy has shifted the dependence from conventional resources to left-over residues. The efficient use of waste biomass is crucial for shaping and building the bio-based

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economy [94]. The gallons of waste generated from the various industrial sector is left unutilized having no economic value. It includes food industry waste, agricultural leftover, leather industry waste, refinery residues, dairy industries effluent, wooden factories waste and tree pruning leftover [93]. The conventional method used for waste management is not much advantageous. In contrast to it, conversion of leftover into value-added products is an upgraded approach. It will add value to waste for the production of desired products exhibiting ecological and economical value [27]. Over the recent past few years, the attempt to reduce pollution caused by waste disposal has boosted the development of treatment technologies for the conversion of waste into biomaterials and bioenergy. The new approach for waste management has the potential to replace conventional fossil fuels with organic biomass for both energy and as well as material (plastics) sources. It will act as an eco-friendly approach and also reduce greenhouse emissions [52]. The organic waste materials act as a renewable substrate for various value-added products like biochemicals and bioethanol. Among the various products generated from industrial organic waste, biopolymers are gaining much more attention owing to their biocompatibility, biodegradability and bio-based origin [34].

Biopolymers are composed of identical units called monomers, synthesized by bacteria, plants, fungi or algae. They have three main categories: polysaccharides, polypeptides and polynucleotides. Being biodegradable in nature, biopolymers mineralize and disintegrate completely into less toxic products, and also they reduce the accumulation of waste in the environment. The advantages of biopolymers include biofunctionality, orderability, biostability, mechanical and chemical properties imparting various applications [77]. The biopolymers have a high cost in comparison to conventional polymers; however, biodegradable polymers derived from a renewable source like industrial waste offers possible alternative because of cost-effectiveness and abundant availability. Most of the organic wastes generated from food and agricultural sectors contain natural biopolymers, both of plant and animal origin [51]. For instance, rotten fruit and fruit juices are rich in sugars like glucose, galactose, fructose and sucrose. The waste generated from mentioned areas can act as a plentiful carbon reservoir for the growth of microorganisms and a pool for the formation of valuable products such as biomaterials [56]. Biopolymers are extracted from waste through valorization and fermentation after pre-treatment of waste feedstock.

The biopolymers generated exhibit application in various fields, including medicines, drug delivery, food packaging, clothing fabrics, cosmetics, agriculture, plastics and other areas [31, 67, 96, 108]. Thus, bio-based polymers could act as an alternative solution for the management of industrial waste as well as waste disposal associated with traditional plastics. Biopolymers can solve the problems of soil and water pollution; also have the capacity to reduce dependence on petroleum-derived plastics. This chapter focuses on the extraction of biopolymers from various types of industrial waste. The unique properties, feedstocks, production, characterization and applications of various types of bio-based polymers are also discussed.

2 Potential Sources of Waste for Biopolymer Production

Waste biomass is a suitable candidate for sustainable and cleaner applications. It overtures attention due to abundance, non-competitiveness for food and problems for proper management. According to the World Bank report if waste mitigation steps are not taken, by 2050 the global waste concentration will hike to 70% of current [44]. The environment being overburdened by both usage of fossil fuel and waste generation paves a way to convert biomass into valuable products. This notion will help in combating environmental problems, reduce dependence on petroleum-derived products and open new revenue generation avenues. With technological advancement and knowledge, it is now possible that all fossil-based materials can be produced from waste biomass [15]. Collaborative steps from various industrial sectors are required to establish biomass utilization technologies.

Biomass is basically the organic content that is produced from biogenic sources and is acting as a renewable resource. There are several types of biomass residues such as the food processing leftover, agricultural residues, wood logging residues, refinery industry residues and leather processing residues [50]. Increasing population has resulted in increased food demand, processing as well as food processing waste. Food wastes, food processing industry waste, dairy industry waste and agro-processing residues pose a serious threat to the environment. According to Food and Agricultural Organization, each year 1.3 billion tons of food waste is generated [70]. The reasons for food wastage can be many, such as poor storage facilities, lack of equipment for harvesting and bad climatic conditions. The food waste includes peels, seeds, pulp, seafood, bran, dairy processing products, stems and shells. All these wastes are a source of biomaterials such as biopolymers having wide applications (Table 1). Fruit and vegetable waste acts as an excellent carbon source for biopolymer production [26]. For example, during the preparation of fruit juices such as apple

Table 1 Biopolymers produced from industrial waste

Biopolymer	Types of waste	Yield	References
Polyhydroxyalkanoates	Jatropha residue	26.06 g/g	[5]
Exopolysaccharide	Cane juice	62 g/l	[91]
Exopolysaccharide	Jute residue	0.297 g/g	[23]
Cellulose	Biodiesel and confectionary residues	13.3 g/l	[105]
Cellulose	Beverage industrial waste	5.7 ± 0.7 g/l	[32]
Cellulose	Fruit juice waste	5.90 g/l	[56]
Cellulose	Distillery effluent	8.11 g/l	[42]
Chitin and chitosan	Food industry waste	0.63 g/l	[20]
Collagen	Fish scale waste	3.1 ± 0.5%	[69]
Poly(4-hydroxybutyrate)	Frying oil	1.2 g/l	[107]
Poly(4-hydroxybutyrate)	Used palm oil	0.8 g/g	[85]

and orange juice, 50% of the fruit is extracted; the rest of the residue contributes to food waste. The leftover residue contains an enormous amount of sugar and a low concentration of proteins also. The above-mentioned bioactive molecules contribute to the production of biopolymers such as polyhydroxyalkanoates (PHA) [86].

Another major type of feedstock provided by agricultural and forestry residue is lignocellulosic waste. It is the most abundant naturally occurring renewable biomass around the globe. It has three major components, lignin, cellulose and hemicellulose, and the other minor components are pectin, lipids, waxes, proteins, ashes and pigments. Lignocellulosic feedstock acts as potential raw material for bioenergy, biochemical and biopolymers [6]. It is usually divided into four categories: agricultural residues, energy crops, forest residues, municipal and industrial waste. Energy crops are low cost, low maintenance, high productivity and short rotation crops. It includes grass, bamboo, poplar, wheatgrass, wood and silver maple. Agricultural residues are usually leftover of commercial crops such as leaves, stems, husk of sugarcane, rice straw, wheat straw and corn stover. Forest residues are waste biomass produced during forest management tasks. Lastly, municipal and industrial waste includes residential waste, commercial waste, institutional waste and waste residues from various industries [61, 89]. The composition of feedstock depends on the type of biomass and plant, and also on the part and age of the plant. The lignocellulosic feedstock can be converted into various high-value products. Most of the leather manufacturing industries and tanneries have serious waste disposal problems as their discarded waste has a diversity of compounds such as solid and liquid waste containing chromium. Interestingly, leather waste also consists of a significant concentration of collagen. Collagen is the most abundant, highly versatile and value-added protein. The collagenic content of leather and tannery waste allows its use for the production of biomaterials, ultimately having wide applications such as in veterinary, cosmetic and medicines [17]. It is also one of the important materials in tissue engineering. Various waste sources for biopolymer production and their applications are depicted in Fig. 1.

3 Biopolymers from Various Industrial Waste

Biopolymers are synthesized by enzyme-catalysed reactions under natural conditions during metabolic processes. Based on the source of biomass, biopolymers are broadly categorized into three major types: natural, microbial-derived and synthetic biopolymers (Fig. 2). Natural polysaccharides include polysaccharides-based biopolymers such as chitosan, starch, alginate, cellulose, agarose, gelatin etc. Owing to the availability and natural abundance of biomass sources, natural biopolymers have gained special attention in past few years. Aliphatic polyesters, polyhydroxyalkanoates, acrylic polymers, polyanhydrides, polybutylene and polycaprolactone are some of the synthetic biopolymers derived from biomass only [39].

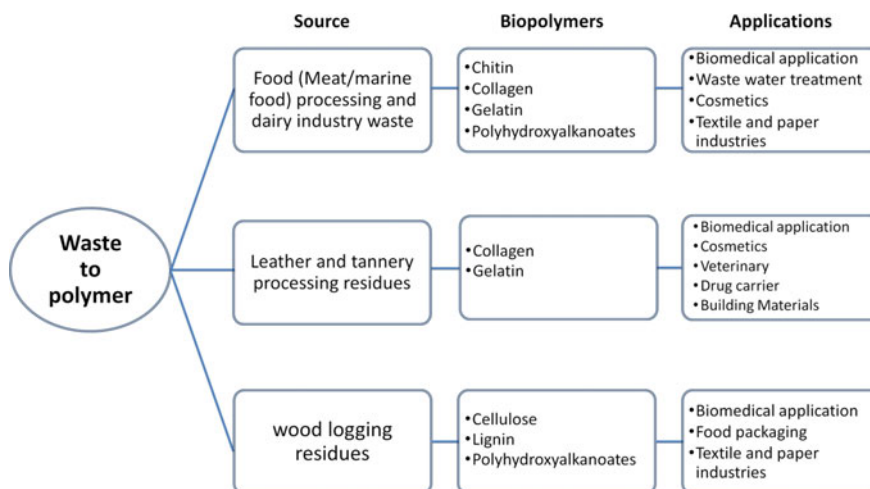


Fig. 1 Waste sources for biopolymer production and their applications

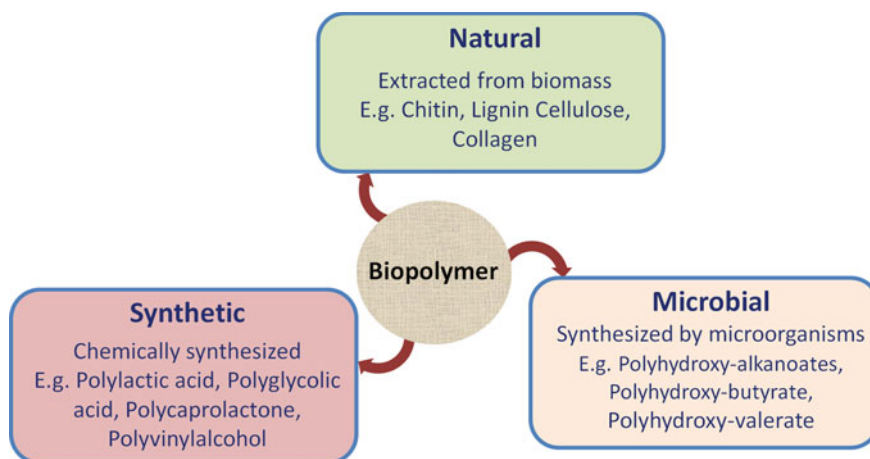


Fig. 2 Classification of biopolymer

3.1 Biopolymers from Food Industry Waste

3.1.1 Cellulose and Hemicellulose

Cellulose is a naturally occurring compound constituting nearly two-thirds of total plant biomass. Cellulose is basically a linear polysaccharide formed of repeating units of β -cellobiose linked by β -1,4-glycosidic linkages. Each cellulose molecule is attached to the neighbouring molecule by a hydrogen bond, imparting enhanced

strength and crystallinity to the biopolymer. It is used for packaging materials such as cellophane [30]. The commercial media used for cellulose production is not considered a feasible method due to high cost and low yield. It leads to the development of a cost-effective method for maximum production yield of cellulose. For the economical method, the prerequisite is the cheap raw material for synthesis. The food industry waste being rich in carbon content acts as an enormous source for cellulose production through the bacterial fermentation process [40]. Fruit pomace has a higher concentration of cellulose, starch and pectin, thereby used as a carbon source for cellulose production. For example, apple has 8.81%, tomato has 8.60% and cucumber has 16.13% cellulose content. During the cellulose production from fruit pomace mild alkali acid conditions are maintained for fractioning of content [103]. In a separate study, coconut and pineapple juices, as waste residue from the juice industry, were used for the formation of bacterial cellulose. Static batch fermentation by three different strains of *Acetobacter xylinum* at 30 °C was used as a method for the production of cellulose. Results showed the higher productivity of cellulose in coconut juice [49]. In another study, *Komagataeibacter xylinus* PTCC 1734 is employed to produce cellulose using cheese whey and date syrup as a carbon source. For the optimization of the process, supplementary agent ascorbic acid was used. The results showed maximum production of bacterial cellulose when an equal mixture of both was used [82]. Sawmill waste is also a potential source for the extraction of cellulosic biomaterial. Hemicellulose is another most abundant renewable material. It forms 15–20% of total lignocellulosic biomass. Being a heteropolysaccharide, hemicellulose is formed of various sugar chains such as mannose, glucose, galactose, xylose and arabinose. These polymers are amorphous structures, having substituent branches that enable them to bond with lignin and cellulose. Hemicellulose forms a bridge with cellulose and lignin by forming hydrogen bonds with cellulose and through the covalent bond to lignin. It results in a rigid structure of biopolymer making it recalcitrant [78]. The cereal straw and sugarcane bagasse after alkali treatment is used for hemicellulose extraction. The presence of alkali in production media aids in the cleavage of lignin and hemicellulose bond, thereby easy isolation of hemicellulose. Banerjee et al. [10] reported the use of pineapple peel waste as an unexplored source of hemicellulose. The maximum recovery of hemicellulose (>95%) was obtained when peel extracted is treated with 15% alkali for 16 h. The extracted hemicellulose was further hydrolysed for the formation of xylo-oligosaccharides (XOS). The XOS-rich liquor can be further used for the synthesis of a chemical like xylitol [10]. Thus, the biopolymers like cellulose and hemicellulose can be efficiently synthesized from cheap raw materials such as industrial waste with additional treatment.

3.1.2 Lignin

Lignin is the second most known abundant biopolymer. It constitutes 15–20% of lignocellulosic biomass. Lignin in association with cellulose and hemicellulose contributes to the structural integrity of plants and thus to timber-built structures. It is an aromatic heteropolymer composed of three monomers: sinapyl alcohol, coniferyl

alcohol and p-coumaryl alcohol. It provides mechanical support to plant cell and makes the cell resistant to microbial attack [58]. Lignocellulosic feedstock from the sugarcane industry such as sugarcane bagasse acts as an excellent source for lignin. The separation of lignin from the other two components of lignocellulosic feed requires certain pre-treatment. The pre-treatment aims to modify or remove the surrounding matrix of lignin through hydrolysis of cellulose. The hydrolysis will convert lignocellulosic feedstock into a form that will facilitate lignin extraction. It is generally extracted in an aqueous solution with ethanol [81]. The isolated lignin can be used for the preparation of lignin nanoparticles which can be further used for the treatment of wooden surfaces. In one such study, lignin was isolated from wood waste, characterized by UV–vis, FTIR, chromatography and GCMS techniques. The isolated lignin is then employed for the fabrication of lignin nanoparticles using the non-solvent method. The produced nanoparticles were subsequently subjected to the dip-coating technique for wood surface treatment.

3.2 *Biopolymers from Marine Seashell Waste*

3.2.1 **Chitin**

The most abundant naturally found biopolymer after cellulose is chitin. It is composed of N-acetylglucosamine units joined by β -(1–4) bonds. It is a functional industrial molecule exhibiting wide application in various fields. Chitin is also considered an important structural component of living organisms. According to the reports, approximately 10^{12} to 10^{14} tons of chitin is naturally produced in the environment; a major fraction is contributed by sea species. The research studies report that per year, total chitin production by arthropods in freshwater is 2.8×10^{10} kg and 1.2×10^{12} kg by a marine ecosystem. Chitin is modified into its derivative chitosan through deacetylation. Both chitin and chitosan are employed in cosmetics, agriculture, medicine and waste treatment. It is a major component of the exoskeleton of zooplanktons such as corals, shrimp, prawns and crabs and also found in the cell wall of fungi [45, 53]. To date, waste biomass from seafood processing industries including crab shells, shrimps and crustacean shells is considered a major source of chitin. The shells are arranged in three components—chitin, minerals and proteins. Chitin in the animal shell provides structural integrity and minerals provide the required strength and support to shells. The presence of proteins in shells makes them living tissue. The industrial processing of crab shells, shrimps and krill for human usage generates an enormous amount of waste (50–60%). The global annual production for this waste is 1.44 million tons. The accumulation of a huge amount of waste and low biodegradability poses a problem for the seafood processing industry. The chemical composition of waste is 20–30% chitin, 30–60% minerals, 20–40% proteins and 1–14% lipids. Thus, marine and sea processing waste acts as an excellent and economical source for chitin [3, 110]. However, the chitin content largely depends

on the environmental conditions and shell species. The traditional chitin extraction technologies operate on high consumption of solvents and energy which, in turn, produce toxic wastes, imposing negative implications on the environment. The cheaper, benign and biological extraction methods of chitin from waste biomass are regarded as a green extraction method. The chitin isolation from exoskeleton such as crustacean shell is both time and energy-saving process. The biological synthesis of chitin involves two major processes—enzymatic treatment and fermentation. During enzymatic treatment, the microbial enzymes are used for deproteinization of shells—a major step of the chemical extraction technique. The solid-state fermentation of waste after deproteinization enables the production of the desired product by reproducing natural microbiological processes. Being a fibrous molecule, chitin is found associated with protein in the form of protein chitin complex and is also found coated with carotenoids and minerals like calcium carbonate. Certain pre-treatment and modification are required for the isolation of chitin from its constituents [43]. In 2012, the study was conducted to investigate the potential of shrimp shell waste for chitin production. The various strains of protease producing *Bacillus* spp. were used for the fermentation of shrimp shell waste. The production media was also supplemented with 5% glucose to promote the demineralization of waste. The extracted chitin was also evaluated for antioxidant activity. The results showed the radical scavenging activity of isolated chitin [35]. Kumari et al. in 2015 reported the isolation of chitin from fishery waste. The extracted chitin was further converted by deacetylation into chitosan. The various characterization techniques like FTIR, X-ray diffraction and scanning electron microscopy confirmed the crystalline nature of both products. The stretching and vibration frequencies in the FTIR pattern showed the formation of alpha chitin [55]. Various studies have been published reporting the potential of prawn waste, crustacean waste, black tiger shrimp waste and other seafood waste for obtaining chitin through microbial enzymatic actions [19, 63, 76].

3.2.2 Collagen

Collagen is an important extracellular protein found in an animal body. It is a highly organized biological macromolecule. It provides mechanical strength and support to various tissue and organs in an animal. Collagen has multiple applications, including usage in tissue engineering, wound management, cosmetics, dental surgeries and orthopaedic. The wide range of applications is attributed to high versatility, biodegradability, easy availability and biocompatibility [59, 95]. Collagen can be obtained from various types of waste such as chicken skin, bovine skin, skin waste of sea organisms like fish, tendons and bone and leather industry waste. Collagen hydrolysate and peptides extracted from seafood waste products have promising medical applications such as skin treatment, blood pressure and osteoporosis. The raw material in the form of waste mostly contains collagen, pigments, lipids, fats, non-collagen material and inorganic material like calcium [65, 75]. The extraction of collagen from waste involves two steps—pre-treatment of waste material followed by

collagen isolation. Before pre-treatment, the biomass is separated into various categories like skin, scales and bone, which will allow contamination reduction and easy separation [74, 88]. During pre-treatment, chemical like EDTA is used for demineralization of bones, sodium chloride, n-butanol and sodium hypochlorite is used for the removal of fats and non-collagenous materials. Finally, collagen extraction can be performed by acid solubilization in the acidic medium containing lactic acid, acetic acid, hydrochloric acid or citric acid. Salt solubilization extraction using sodium chloride can also be used for obtaining collagen from seafood. Acidic and salt solubilization methods have certain limitations in terms of low yield. To achieve maximum yield of collagen from waste, enzymatic hydrolysis after pre-treatment is considered an excellent approach. The enzymes like trypsin, pepsin, collagenases and papain are employed under various environmental conditions (e.g., pH and temperature) for efficient extraction of collagen. Additionally, ultrasonication for the digestion and isolation of protein can also be the method for obtaining collagen [2]. Ferrario and co-workers reported the isolation of collagen from the food waste of sea urchins. The extracted collagen is further used as a skin graft in the form of a scaffold during injuries and wound repair [33]. In another study, trimming waste of leather industry is used as a raw material for the extraction of collagen. The trimmings are rich in fibrous proteins, thereby acting as a valuable resource for collagen. The study was conducted in acetic acid and propionic acid for the solubilization of collagen. The results showed 85% of the collagen in acetic acid treatment and nearly 93% in propionic acid. The isolated collagen was characterized using infrared spectroscopy, circular dichroism and SDS-PAGE. Based on the results, it was concluded that type I collagen was present in trimming waste. Therefore, trimming waste acts as a cheap source of collagen, displaying application in biomaterials, pharmaceutical and tissue engineering [65].

3.2.3 Gelatin

Gelatin another biopolymer is obtained from the skin, bones, tendons and cartilages of animals. It acts as an excellent bioactive compound exhibiting pharmaceutical and food packaging applications. The research report publishes the isolation of gelatin from scale waste of fish called Black tilapia. The demineralization and acid treatment of waste was performed before the thermal extraction of gelatin. The scales waste produced 11.88% of gelatin, indicating scales as a possible source of gelatin extraction. Further, FTIR was used for the characterization of isolated gelatin [99].

3.3 *Biopolymers from Wood and Paper Mill Waste*

3.3.1 Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are naturally occurring biodegradable polymers isolated from microorganisms. They are found deposited inside the microbial cell as carbon and energy source. The biocompatibility and biodegradability make them better commercial polymers exhibiting properties of plastics. The commercial production of PHAs is comparatively low due to costly raw materials. Recent trends are shifting toward the usage of waste as feedstock for PHA formation. Also, more than 300 species of microbes are known to have the ability to synthesize PHA [22, 48]. The various controllable factors like bacterial growth, type of cultures, cell density, process pH and temperature enable the desired and economical production of PHAs. The industrial, household and agricultural wastes being rich in organic matter serve as a potent source for PHA extraction. The waste generated from mills, like during palm oil extraction, mining operation, biodiesel production, wood and paper industry, provides the potential raw material for obtaining PHA. In addition, agricultural wastes like crop residues, vegetable oils, animal fats and molasses rich in organic compounds are prospective substrates for PHA production. The other waste feedstock for PHA production is biodiesel liquor waste containing glycerol and whey permeate which are also used for PHA production [16, 73]. PHA from waste can be synthesized by single as well as mixed cultures. The few known commercially synthesized PHAs by pure cultures are Biomer, Biocycle, Biopol and Nodox [66]. However, mixed cultures are more advantageous than pure cultures because they utilize a wider range of waste substrates, making the process more efficient. Bhuwal and co-workers reported the isolation of PHA accumulating bacteria from the paper and pulp industry and further poly(3-hydroxybutyrate) (PHB) production from cardboard industry waste [12]. In 2015, a study reported the generation of PHA by *Bacillus* sp. isolated from wastewater. The various growth conditions for microbe were optimized, and under optimal conditions 3.09 g/l of PHA was produced by the microbe. The NMR and FTIR were used for characterization and detailed insight into the structure of isolated PHA [68]. Shah and Kumar also conducted the study for the isolation of PHA producing bacteria. The isolated bacteria exhibited potential to generate PHAs from various agro-industrial wastes, including fruit pulp, kitchen waste and sugarcane molasses. The results showed that 44.5% of PHA is from kitchen waste. Further, XRD and FTIR were used for the analysis of produced PHAs [92].

3.3.2 Poly(3-hydroxybutyrate)

Poly(3-hydroxybutyrate) is a homopolymer of 3-hydroxybutyrate, a biodegradable thermoplastic biopolymer of PHA. The molecular weight of PHB ranges from 2000 to 4000 kDa. It largely depends on the amount of biopolymer accumulated by microbe

during synthesis, which in turn depends on cell growth density and growth conditions. Being biodegradable, biocompatible and thermoplastic, PHB is an excellent substitute for conventional plastics and polypropylene [84]. The utilization of waste biomass and sustainable resources is considered as promising substrates for PHB production. Lignocellulosic biomass, dairy industry waste, starch-based biomass, sucrose-based material, fats, glycerol, and oil-containing residues are the potential raw materials for PHB synthesis. All the mentioned biomass materials are organic-matter-rich residues containing carbon sources, proteins, lignin, cellulose, lactose and salts, thereby acting as an abundant and cheap raw substrate for PHB synthesis [11]. The complex composition of waste biomass containing starch, sugar and cellulose requires pretreatment before its conversion into biopolymers. Various pre-treatment strategies like chemical mechanical hydrolysis, acid or salt treatment, enzymatic action and ultrasound-assisted enzymatic hydrolysis are commonly employed for easy manufacturing of PHB from biomass. The pre-treatment is basically used for delignification, desaccharification, cleavage of bonds (glycosidic, ether and ester) for modification of complex molecules to monomers. After the pre-treatment stage, fermentation of biomass residues is performed for the production of PHB by bacteria. Batch, fed-batch, solid-state fermentation and submerged fermentation are some of the fermentation techniques commonly employed for PHB production [64]. Various microbial species like *Bacillus* sp., *Methylobacterium* sp., *Alcaligenes* sp. are reported as PHB producers through fermentation of waste biomass. Biogreen is one of the commercially known PHB, manufactured by Japan [84]. Silva et al. published a research report for PHB synthesis from extraction waste. The *Spirulina* sp. LED 18 was cultivated to produce PHB at various concentrations of waste. The results confirmed the 10.6% production concentration of PHB by microalgal biomass [25]. Further for optimization and enhanced production of PHB, various studies have been conducted in terms of effective pre-treatment of biomass. Saratale et al. assessed the effect of alkaline and assisted ultrasound treatment on wheat biomass for increased enzymatic saccharification of biomass into monomers. The results showed that at optimum conditions, the combination of NaOH and ultrasound treatment resulted in 84.5% hydrolysis, 70% delignification, 65% xylose yield and 90% glucose yield. The pre-treatment results were confirmed by FTIR, SEM and XRD, revealing destruction of the ultrastructure of biomass, thus improving accessibility of enzymes. Further, the enzymatic hydrolysates were used for PHB production. The results suggested the excellent yield and standard properties of extracted PHB [90]. As PHB is an important commercial biopolymer, the mechanical properties of PHB can be further enhanced by forming its blend with polylactic acid and reinforcing it into cellulosic nanofibrils [7].

3.3.3 Polyhydroxy-valerate

Polyhydroxy-valerate (PHV) is a copolymer of PHB, formed by co-feeding of an additional substrate, resulting in biopolymer with more pronounced properties. The incorporation of 3-hydroxy-valerate into PHB results in the formation of complex

poly-3-hydroxybutyrate-co-3-hydroxy-valerate P(3HB-3HV). The complex formed has low crystallinity, low melting temperature and high elasticity, making it suitable for the formation of fibres and films with varying elasticities. BIOPOL is one such commercially known copolymers of P(3HB-3HV) used for film production, packaging, paper boards and coat paper [80].

3.4 Polylactic acid

Polylactic acid (PLA), also known as polylactide, is a thermoplastic aliphatic biodegradable polymer. It is synthesized either by polymerization or condensation of its monomers—lactic acid, a product obtained by fermentation of carbohydrates. Being a biocompatible and green polymer, PLA has numerous applications such as the synthesis of packaging material, foams and fibres [71]. The utilization of economical, non-food substrates like food waste, agricultural waste and lignocellulosic waste has favoured advanced and low-cost production of PLA and its polymer. The high carbohydrate content of food waste including refused food, kitchen residues, vegetable peels and unsold bakery products are appropriate substrates for the fermentation and PLA synthesis. Also, the carbon-rich starchy and sugary substrates such as sugarcane molasses, corn starch are some other favourable materials for PLA synthesis [97]. For the efficient production of PLA, abiotic factors like pH, carbon–nitrogen content, temperature, sterilization, organic content need to be optimized. In addition to optimization, appropriate pre-treatment methods depending upon the nature of substrate is also considered. The various options for pre-treatment are physical and chemical methods, alkali and acid treatment, enzymatic hydrolysis, steam-based and combined methods such as microwave-assisted can be employed. Dhandapani et al. reported the research study for the formation of lactic acid from wastepaper sludge. *Rhizopus* sp. was used for fermentation under optimized environmental conditions. The results showed 27 g/l of lactic acid production by cellulase enzyme [28].

4 Application of Biopolymers

Biopolymers are known to cover a significant portion of day-to-day life products, particularly food, agricultural, medical, pharmaceutical and goods packaging sectors. Various types of biopolymers, with examples and applications, are mentioned in Table 2. Most importantly being thermoplastic biodegradable material, they can replace conventional petroleum-based plastics [106]. The biomedical application of biopolymers has drawn considerable attention in comparison to other sectors because they have high entity significance. In the medical field, biopolymers are used for wound healing, tissue engineering, scaffold designing, oral surgeries, drug delivery and regenerative medicines [54]. Chitin and its derivative chitosan are known as an

Table 2 Biopolymers from industrial waste and their potential applications

Industrial waste biopolymer	Biopolymer	Applications	References
Natural biopolymers	Starch	Food packaging, antimicrobial, biomedicine	[18, 21, 38, 41, 46, 47, 79, 98–100, 102, 104]
	Cellulose	Food additive, paper industry, wound healing	
	Hemicellulose	Biomedical, food coating, packaging, membrane materials	
	Chitin	Medicines, water treatment, paper industry, textile industry, wood industry	
	Chitosan	Agriculture, biomedicine, cosmetics, cement	
	Collagen	Drug delivery, food industry, leather production, cosmetics	
	Gelatin	Tissue engineering, food industry	
	Xanthan gum	Agriculture, medicines, cosmetics, oil recovery	
	Pectin	Biomedicines, drug delivery	
	Hyaluronic acid	Cosmetics, drug delivery, wound healing	
Derivatives of natural biopolymers	Methylcellulose	Cosmetics, drug delivery, construction material	[1, 4, 13, 14, 37, 62, 101]
	Carboxymethylcellulose	Textiles, paper, pharmaceutical	
	Cellulose acetate	Textiles, film media	
	Acetylated hemicellulose	Hydrophobic molecules, films	

(continued)

Table 2 (continued)

Industrial waste biopolymer	Biopolymer	Applications	References
Industrial waste biopolymer	Nanocrystalline cellulose	Gels, adhesive, membrane materials	
	Carboxymethyl chitosan hemicellulose	Wastewater treatment	
	Esterified hemicellulose	Antimicrobial, film-forming agent	
	Organosolv lignin	Thermostable molecule	
	Lignosulfonate	Food, cosmetics, antioxidant	
	Kraft lignin	Corrosion inhibitor	
Synthetic biopolymers	Polylactic acid	Food packaging, containers	[8, 9, 57, 60, 109]
	Polycaprolactone	Bone scaffolds, food industry	
	Polyvinyl alcohol	Medicines, paper processing, emulsifier, textiles	
	Polyhydroxybutyrate	Biomedicines, disposable films	
	Polyglycolic acid	Pharmaceutical, medical devices	
	Polyvinyl chloride	Packaging material, films	

excellent bioactive biomaterial which are currently being used for the purpose of wound healing, rapid dermal regeneration, orthopaedic and periodontal treatments. The research study reports the production and modification of bacterial cellulose because of its diverse application in medicine, including regenerative medicine, wound healing, blood vessel, cartilage repair, bone implant, dura matter prosthesis and nerve surgery [87]. The biocompatible, non-genotoxic and non-cytotoxic nature of cellulose imparts it a wide range of applications. Similarly, collagen has also been reported to be an excellent candidate possessing biomedical applications like tissue engineering, drug delivery and orthopaedic defect. Many polysaccharide and protein-based biopolymers have also been reported for their antimicrobial and antioxidant properties [24]. Synthetic bioplastics are also drawing attention in medicines, particularly for vascular grafting, surgical implants of dental and orthopaedics, being as surgical sutures. Biopolymers are also extensively utilized as a promising alternative to traditional plastics for food packaging. These are used in combination with various other materials to ensure the quality, safety and storage of food products during their packaging. It enables long-term usage of food products by enhancing their shelf life, thereby preventing deterioration and massive loss of valuable food items. Polyethylene, polylactic acid, starch cellulose, pectin, gelatin and collagen are some examples of green polymers used for food packaging [31, 36]. In addition, biopolymers in the food industry are also used for coatings, freezing of juices, texture properties, food processing and antimicrobial and antioxidative material carriers. Biopolymers like starch, cellulose, chitosan, gelatin are also used for the synthesis of nanomaterials, for water purification, automotive sectors for designing minimal fuel intake vehicles and in the agricultural domain for soil-enhancing properties [29, 72, 83].

5 Conclusion

The management of wastes generated from various industrial sectors is a major environmental concern. The harmless and sustainable waste disposal approach for converting waste into valuable materials is gaining interest. The microbial technologies for these valuable feedstocks will generate renewable and green sources such as bioenergy and biomaterials. Biopolymers synthesis from the valorization of waste feedstock is one such approach for the generation of high value-added materials. The chapter has highlighted various potential waste biomass sources for the green synthesis of biopolymers and the process parameters for efficient production. The formation of biopolymers from waste will help to remediate the environment in terms of waste management, reduction of greenhouse gases and dependence on non-renewable sources. Another application of biopolymers is the reduced dependence on conventional petroleum-based plastics through the usage of synthetic biopolymers. These biopolymers have several applications in medicines, agricultural products, wastewater treatment, food packaging, cosmetic preparation, automation and electronics. Thus, the formation of valuable materials from low cost, abundant and unused raw materials is a smart and green approach. It will arise as a key measure for the

remediation of waste as well as the synthesis of valuable biomaterials. The biodegradability and biocompatibility of biopolymers will encourage its more usage. For the more efficient production and application, the prospects for biopolymers synthesis can be its increased scalability through its transition from lab scale to industry-based pilot production. Additionally, the detailed investigation of models and their process conditions will aid in employing these technologies as green solution for environmental sustenance.

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Biopolymers from Microbial Flora



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Abstract Over the recent times with the increasing interest on the environment, every country is trying to utilise every product from a natural resource in a needful manner. Bio-based polymer or biopolymer describes that they are from all plant, animal or microbial origin. With the advancing technology, consumers are also welcoming the synthetically originated polymers which are environment friendly. Biopolymers provide a plethora of applications in the various fields as they possess certain properties like biocompatibility, biodegradation to non-toxic products, low antigenicity, high bio-activity, processability to complicated shapes with appropriate porosity apart from ability to support cell growth and proliferation. In the present chapter an emphasis on biopolymers from microbial flora having applications in cosmetic, pharmaceutical and biomedical, agriculture, food etc. has been presented. Biopolymers are most commonly used and are most abundantly available and they provide protection against biotic stress. A combination of biopolymer and nanotechnology is a novel area of research paving way for nanomedicines and can be exploited for their potential application in drug delivery and gene therapy. The application in cosmetics and medicated cosmetics is also being researched. The research required to understand the novel applications of biopolymers cannot be limited to a specified field since they are employed in diverse areas. With the present day available literature, future work should focus on bioavailability.

Keywords Biodegradable · Biomedical applications · Polymers · Drug delivery · Microorganisms

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1 Introduction

Biopolymers are natural polymers which are obtained from natural sources like plants, microflora etc. or we can simply call them as the polymers that are extracted from the cells of living organisms under natural conditions of their growth cycles. Every year around the world approximately 140 million tons of polymers are produced synthetically. These synthetic polymers are causing environmental pollution during their degradation process. Some synthetic polymers cause water pollution as some of them get dissolved in the water. Plastic and polymers have become integral part of our basic life. Due to their stability, these plastic or polymers will take long time for degradation and hence when they are left as such in open areas or landfills, they cause land or soil pollution. Since the synthetic polymers are causing pollution the attention is growing towards a clean and eco friendly polymer. Some studies also suggest that they are minimize the use of fossil fuels and are thus replacing the petroleum based polymers. The monomeric units held together by covalent bonds will form long chain or larger molecules and hence called as polymers [1]. Synthesis of nanocellulose from rubberwood fibers via ultrasonication was reported by Poddar [2]. Sharma and Gupta [3] discussed about the sustainable management of keratin waste biomass. Within the living cells these polymers are produced by complex metabolic pathways. However, their limitation includes poor mechanical properties, low shelf life, sensitivity to chemicals, poor durability and limited processing capacity. These limitations and can be overcome by introducing the nanofillers resulting in the formation of biocomposites or otherwise called as bionanocomposites. Some of the areas where these bionanocomposites are used are medicine, cosmetics, food and packaging, pharmaceuticals, electronics, agriculture etc. These biopolymers can be produced chemically or by organic methods from various sources [4]. Sharma et al. [5] studied the different treatment methods for chicken feather biomass. Characterization of keratin microparticles from feather biomass with potent antioxidant and anticancer activities was also reported [6]. Investigation of extraction parameters of keratin from chicken feather using Design-Expert was reported by Kamarudin et al. [7]. Generally biopolymers can be produced from animals, plants and microbes. Using the raw materials from these natural sources, producing these polymers contribute to the sustainable development [8]. Microbes forms one of the important sources for the extraction of biopolymers. Kumaran et al. [9] synthesised wound-healing keratin hydrogels using chicken feathers proteins. Unlike synthetic polymers the biopolymers do not have impact on the environment in the process of degradation. Sharma et al. [10] have described an efficient method for conversion of waste feather keratin into ecofriendly bioplastic film. Bioplastic film from Keratin was described by Ramakrishnan et al. [11]. Products like cellulose, starch, hydrocarbons polysaccharides like xanthan, pullulan, curdlan, chitin, chitosan, hyaluronic acid etc. can be isolated from bacterial and fungal sources. The process of breakdown of natural polymers can be either aerobic or anaerobic [8].

1.1 *Functions of Biopolymers*

These biopolymers that are synthesized from various microbes fulfil a wide range of essential function for the organism. They help the microbial cell to adapt to the changing environmental conditions and survive and multiply. Some of them include.

- (a) To conserve and to express the genetic information.
- (b) To participate in catalysis reactions of the cell.
- (c) To store the energy, nutrients etc.
- (d) Act as a source of carbon.
- (e) Defending the organism from other predators, and also to protect the cell from environment, by identifying the biotic and abiotic factors.
- (f) The produced biopolymers act as a mediator for communication with other organisms and to send and receive signals within the environment surrounding it Madigan et al. [12].

1.2 *Synthesis of Biopolymers*

Biopolymers can be produced in several ways from different sources like plants, algae, bacteria and fungi.

- (a) From natural environments: Some of the biopolymers like agar, alginates are extracted from the algae (e.g. Gelidium, Gracilaria) which are found in the natural habitats by alkaline treatment followed by purification. Polysaccharides like hyaluronic acid are isolated from the new born umbilical cords. The precursor substrates will be taken from the environment by the bacterial cell, with the help of enzymes from the metabolic pathway resulting in the activated precursors and secretion of the biopolymers.
- (b) In-vitro synthesis using enzymes: Nucleic acids like DNA or RNA can be synthesized by in vitro techniques like PCR (Polymerase Chain Reaction). The methods require a heat stable enzyme. On the other hand, using suitable enzymes such as dextran sucrose, polysaccharides like dextrans can be synthesized.
- (c) Fermentation: This method is mostly employed for the large scale production in industries using biotechnological advancements specifically for some polysaccharides like polyhydroxyalkanoates, glycogen, starch that occur intracellularly and alginates, dextran, xanthan, curdlan, pullulan, chitosan that occur extracellularly. For the natural polymers that are produced inside the cell, the limiting factor is the space in the cytoplasm of the cell. Furthermore, after the reaction the cell needs to be broken to extract it followed by purification which involves several steps in the process. And hence the yield is low when compared to the one secreting it outside the cell. The fermentation process requires the addition of enzymes to the bioreactor ensuring the specified incubation time using parameter like temperature, pH etc. The product will be collected and

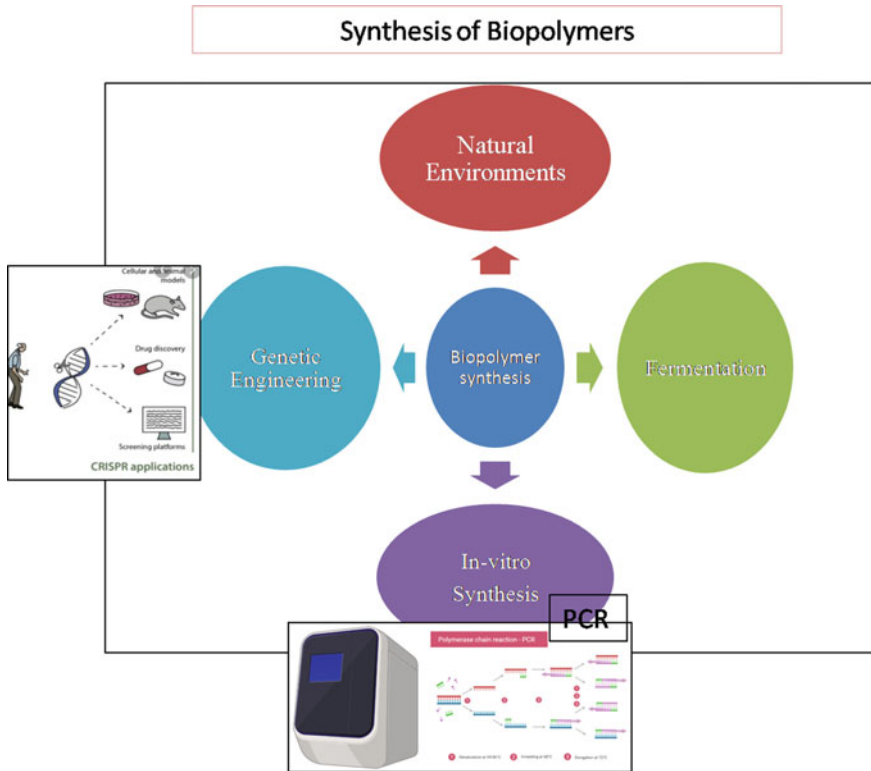


Fig. 1 Synthesis of biopolymers from Microflora

chemically processed to get it in the pure form. Examples of polymers that can be synthesized by using such methods are polylactic acid, poly β -D-glutamate [13].

- (e) Genetic engineering: The method can be applied for the synthesis of the protein polymers, as we all know that genetic engineering offers revolutionary tools to manipulate the gene and its expression. Using recombinant DNA technology polymer chain of the uniform length and composition can be constructed [18]. In the present communication we tried to review all the biopolymers from microflora i.e. from bacteria, fungi and algae along with their applications (Figs. 1, 2 and 3).

2 Bacterial Biopolymers

Bacteria are considered as one of the prime sources for the synthesis of the both intracellular and extracellular biopolymers. The bacterial biopolymers can be classified as polysaccharides, polyesters, polyphosphates and proteins. These biopolymer

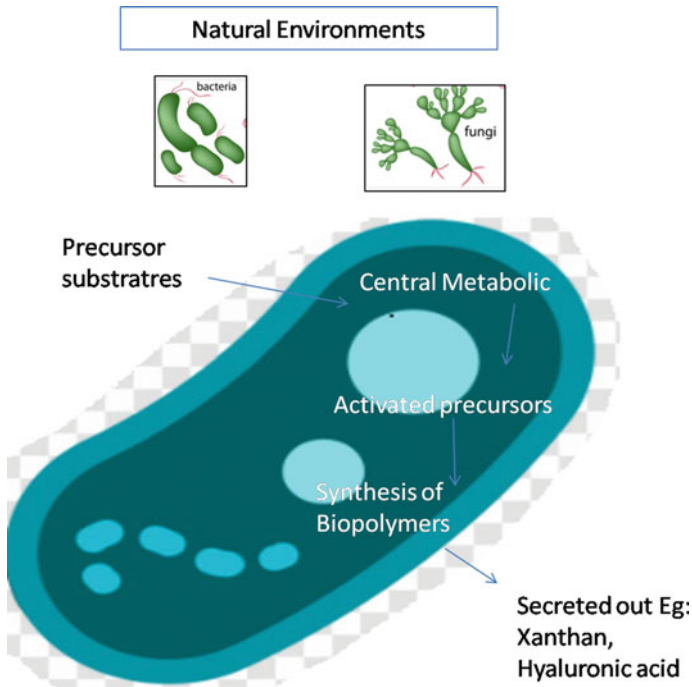


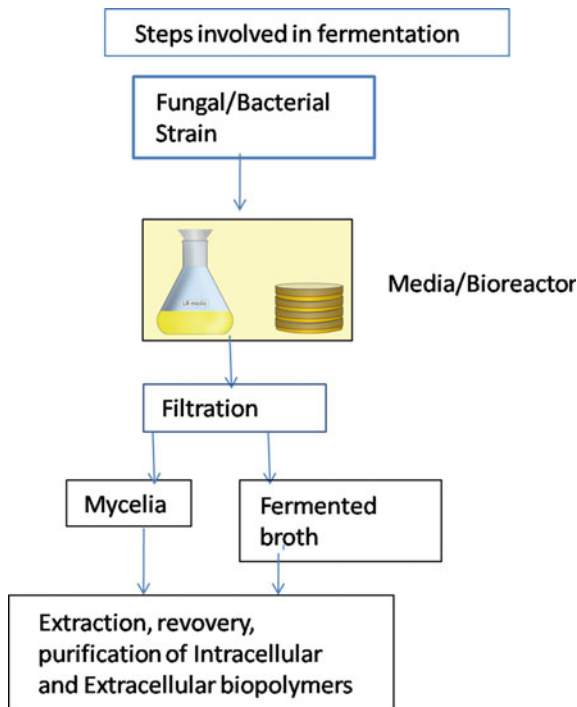
Fig. 2 Synthesis of biopolymer in the bacterial Cell

substances in bacteria function as storage material, as capsule protecting the bacteria, as a component of the extra cellular matrix or biofilm. However, each of the biopolymer has its own commercial significance in medicine, industry, food etc. which is dependent upon the chemical and material properties. The synthesis of polymers is a energy dependent process, but with bacteria they can be produced even in unfavourable conditions [14].

2.1 Polysaccharides from Bacteria as Biopolymers

Polysaccharides are polymers of monosaccharide residues which can be further classified as hetero or homopolysaccharides based on their composition. These also can be charged or uncharged, branched or unbranched depending upon the complexity. This structural complexity gives the polysaccharides unique properties enabling them with varied diverse functions. Several bacteria secrete these polysaccharides as capsular polysaccharides, exopolysaccharides and intracellular polysaccharides. The capsular polysaccharides is found associated to the cell surface [15]. Glycogen is mostly found as capsular polysaccharide. Alginate, cellulose and hyaluronic acid (Table 1) form different types of exopolysaccharides. E.coli secrete

Fig. 3 Steps involved in the fermentation



phosphoethanolamine [16] and other types of heteropolysaccharides are produced by *Bacillus* and *Streptococcus* [17]. *Nesseria* produces capsular homo polysaccharides consisting of NAM and silalic acid [18]. The synthesis of sugars is a costly process hence bacteria serve as excellent source for these polymers. Due to the hydroxy and carboxyl groups on these polysaccharides they have good water binding capacity with increased intermolecular interactions and cross linking. The polymers of sugars also can form hydrogels and thus act as important mediators in the drug delivery, enzyme immobilization, tissue engineering, therapeutics etc. [19]. Hyaluronic acid is used in the treatment of arthritis. It is administered as an injection into knee joints. The presence of additional groups like acetyl improve the structure and properties of the polysaccharides and conferring viscoelasticity, solubility, molecular weight, intra chain interactions, water holding capacity [20]. Hydrogels made from cellulose are widely used in biomedical applications such as for dressing the wounds [21]. Cellulose from *Komagataeibacter xylinus* (Table 1) have been largely used in textile industry for the manufacture of rayon fibre which is used as clothing [22]. The other important application of bacterial cellulose is, it is the basic substrate for the paper and pulp making. Over the recent years, the bacterial cellulose produced by fermentation is replacing the cellulose from plant to prevent the deforestation [23]. Cellulose in combination with the carbon nanotubes is used in supercapacitor electrodes, electromagnetic interference shielding units and also as a sensor monitoring the water and pressure [24]. Xanthan a heteropolymer produced from the *Xanthomonas campestris*

Table 1 Bacterial polysaccharides, source and their function

S. no	Bacterial polysaccharide	Source	Function	References
1	Alginate	<i>Pseudomonas aeruginosa</i>	Hydrogels, Drug delivery, Tissue Engineering	[31]
2	Cellulose	<i>Komagataeibacter xylinus</i>	Textile Industry, Paper, nanotubes	[22]
3	Hyaluronic acid	<i>Bacillus cereus G9241 (P)</i> and <i>Streptococcus equi</i>	Treatment of arthritis	[17]
4	Xanthan	<i>Xanthomonas campestris</i>	Oil recover, Mineral ore extraction	[32, 33, 25]
5	PolyLacticacid (PLA)	<i>Bacillus coagulans</i>	Agriculture, cosmetic and personal hygiene, medical and tissue engineering	[34]
6	Homopolysaccharides of NAM and sialic acids	<i>Nisseria</i>	Hydrogels, Drug Deliver, Tissue Engineering	[18]
7	Heteropolysaccharides, PEP	<i>E.coli, Bacillus and Streptococcus</i>	Hydrogels, Drug Deliver, Tissue Engineering	[16, 17]

(Table 1) consists of five different sugar residues. The important application is found in the oil recovery and mineral ore extraction. It also has been widely used in the paper manufacturing process as a modifier, in agriculture it is applied as plant growth stimulator. Other applications include in food sectors as a gelling agent in pudding, ice-cream, cheese, cosmetic and even in pharmaceuticals [25]. Dextran, a polymer of glucose is polymerised in the presence of enzyme dextran sucrose. It has many medical applications like treating the wound, as sutures in surgeries, blood volume and plasma expanders, treating vascular occlusion, anemia treatment etc. [26]. Poly-lactic acid (PLA) (Table 1) is another important biopolymer that is renewable and biodegradable, having biocidal activity and is one of the most widely used alternative to the petroleum based polymer. It has got its applications in the fields of packing industry, agriculture, cosmetic and personal hygiene, medical and tissue engineering [27, 28]. A combination of nonmaterial and polymer results in the formation of bionanocomposites with enhanced material properties. Transparent nanocomposites were prepared by adding the PEG (Poly ethylene glycol) to PLA [29]. This addition improves the thermo mechanical properties of the biopolymer. It was understood and analysed in the studies by Zhao et al. [30] that PLA on combination with stearic acid-MgO modified preparation was having enhanced compatibility in the cell and is thus promoting cell proliferation and matrix activity.

2.2 *Bacterial Polyamides as Biopolymers*

Polyamides are the polymers of the amino acids secreted by bacteria like *Bacillus licheniformis*, *Bacillus megaterium* and most cyanobacteria [35]. These are highly biodegradable, non toxic and can be renewable. These include poly γ -d-glutamic acid (γ -PGA) which is used as a flocculant replacing the synthetic flocculants like poly aluminium chloride in treating waste water, they also have got biomedical and bioremediation application and used in the hydrogel preparation [36]. Poly ϵ -l-lysine (ϵ -PL) has got antibacterial or bacterial static properties [37] or the intracellular cyanophycin, a copolymer of L-aspartic acid and L-arginine. They contribute for industrial applications [38, 39].

2.3 *Polyesters of Bacteria as Biopolymers*

Poly (R-3-hydroxybutyrate) that is classified under Polyhydroxyalkanoates (PHA) is synthesized as linear polyesters that is packaged in hydrophobic spherical inclusions. PHA can act as terminal electron acceptors in the absence of oxygen (electron acceptor in the anaerobic conditions). Example of bacterium producing PHA is *P.aeruginosa* [40]. PHA can be used to make biomedical materials like sutures for hospitals, in tissue engineering and as carriers of drugs as they enhance the properties [41]. PHA on coating with proteins of interest contribute as being vaccine, resins that can be used for separation or purification, in immunodiagnosics, as enzyme carriers and also play important role in recombinant protein synthesis [42, 43]. Reinforcement of saw dust from wood coupled with CaCO_3 and acetyl tributyl citrate as a filler into polyhydroxybutyrate resulted in improving the resistance. The filler also accelerated the degradation of polymer in an ecofriendly manner and thus is occupying a place in the agriculture and plant nursery [44]. The heat resistance nature, stiffness, strength are enhanced by cellulose and thermoplastic polyurethane that has been added to poly 3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) another widely used polyester biopolymer [45]. The strength of the combination is tested under various conditions and is found to be of uppermost value [4].

2.4 *Bacterial Polyphosphates as Biopolymers*

Inorganic phosphates condensed ranging from three to several hundred give rise to polyphates. These are highly negative charged and consist of anhydride bonds hence, function as energy storage polymer storing phosphate. They also act as a buffer against alkali, and as a metal chelator and aid the channel complexes in DNA uptake [46, 47]. Polyphosphates are considered as a boon in regenerative medicine. They are used in the cartilage and bone repair for delivering drugs. Considering their efficiency

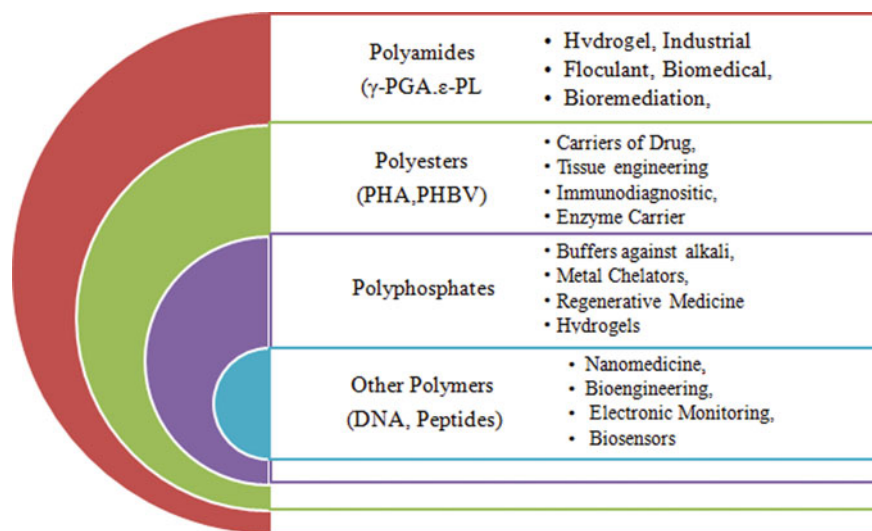


Fig. 4 Sources and applications of polyamides, polyphosphates, polyesters

they are used to drive the energy consuming enzyme catalysed reactions. The remarkable ability of the polyphosphates to interact with the positively charged polymers like glutamate and hyaluronic acid, or inorganic cations like calcium, magnesium etc., or with the organic molecules like amino acids, peptides they are prepared as hydrogels for bone mineralisation [48–50]. This ability of them allows them to be categorised as smart biomaterials enabling them to be used as bioink in regenerative medicine [51]. Bacteria belonging to the genus *Mycobacterium* and *Corynebacterium* are the unique sources for the polyphosphates [52] (Fig. 4).

2.5 Other Polymers of Bacteria

Other Biopolymers from the bacteria include extracellular DNA, proteins. The extracellular DNA from *Pseudomonas aeruginosa* can interact with the polymers of sugars, and cations. The proteins due to their different amino acid composition can be arranged to form nanotubes or nanofibers. The formation of these precise features renders to the high surface area to volume ratio enabling them to form multilayer lattices that have application in bioengineering and nanomedicine [53, 54]. DNA and protein can make the great genetic tools that can be engineered to different ways yielding products from microbes like gadgets for electronic monitoring, biosensors, bioremediation etc. [55, 56].

3 Fungal Biopolymers

Biopolymers from fungi have received attention due to their biological and physicochemical properties like a renewable source and for biocompatibility. They have got wider applications in food industry as emulsifiers, in agriculture as surfactants, chemicals, medicine etc. [57]. Recent studies by Donot et al. [58] suggested that fungi can produce a polymer even at a concentration of 40 g/L or higher than that Donot et al. [58]. Some of the most widely used fungal polymers include Pullulan, Scleroglucan and L-malic acid etc.

3.1 *Fungal Polysaccharides as Biopolymers*

Polysaccharides, found in various sources like bacteria, fungi, plants, animals form the most abundant group that are equipped with special characteristic features. Polysaccharides from fungi are also called gums. These get dissolved in water or other aqueous liquids easily therefore called as hydrophilic. Due to this property the viscosity is increased [59]. The secreted polymers can be categorised as intracellular and extracellular [60]. The fungal exopolysaccharide and cytoplasmic layer of polymers of sugar of cell wall consists mostly of branched repeated units of glucose, fructose, mannose and galactose etc. [61]. Heteropolysaccharides have varied sugar units, where as homopolysaccharides in most cases contain the sugar residues glucose, mannose and their monomers. Occasionally xylose, rhamnose, arabinose, fructose are also found. Some of the important applications of these biopolymers of polysaccharides include antimicrobial, antitumor, antioxidant activity. In medicine they act as “hepatoprotective” protecting the liver, modulators of immune system and also prone to have “hypoglycemic” (decreases the sugar in blood) activity [62]. Studies on species *Lasiodiplodia* (Table 2) suggest that the EPS layer is made of sugar residues, glucose and mannose and is prone to antibacterial and antifungal activities. The activity varies with the molecular weight, composition of sugar residues, conformation, configuration of the bonds between sugar molecules and extraction methods [63].

3.1.1 Glucans

Glucans are generally polymers of glucose residues linked by glycosidic bonds. They are found in the fungal cell wall. They mostly contain glucose residues as monomers and are held together by α or β type of glycosidic bonds. Their structure contain the linear or branched chains and they may be found as fibrillar or amorphous in state [71, 72]. Glycogen from fungi is an example of glucan that is amorphous and is soluble in hot aqueous solution. The most abundant glucan is β - glucan which consists of a complex structure favouring crystalline structure resulting in microfibrills and is

Table 2 Biopolymers from fungi

S.no	Fungal polysaccharide	Fungal source	Function	References
1	β glucans	Lentinus edodes, Schizophyllum commune, and Grifola frondosa, saccharomyces cervisiae	Antitumor property, Bioemulsifier, Food additive, pharmaceutical	[64–67]
2	EPS	Lasiodiplodia	Antibacterial, Antifungal, anti tumor, anti inflammatory, modifiers of immune system	[63]
3	Pullulan	Aureobasidium pullulans	Food, agriculture, textile industry, cosmetic and pharmaceutical	[68, 69]
4	Scleroglucan	Sclerotium species	Oil recovery, food, cosmetics, pharmaceuticals, Biotechnology	[70]

insoluble in water or any other common solvents of sugars [72]. β -glucan in combination with the mannoproteins are shown to have remarkable properties. They are giving promising results as effective bioemulsifiers. β -glucan have got the potential to form stable emulsions with vegetable oils and is occupying a place as food additive and in other pharmaceutical applications [73]. The ability of β -glucans to solubilise in water, its viscosity, and the capacity to form gels is conferring it to be an important biopolymer of food, cosmetic and pharmaceutical industry [74, 75]. One of the common source of the glucan is (Table 2) Saccharomyces cervisiae. These contribute to around 1–14% of the dry weight of the cell in fungi. The most common method of extraction is by alkali treatment. Glucans also are resistant against radio waves and have the potential to treat several diseases [64–66]. The other sources for the isolation of β glucans, are Lentinus edodes, Schizophyllum commune, and Grifola frondosa (Table 2). The glucans form these sources are having different branching points and hence have different structures and are said to possess antitumor property.

3.1.2 Pullulan and Scleroglucan

Pullulan is a polysaccharide consisting of maltotriose residues. The glucose units of maltotriose are held by α 1-4 and α 1-6 glycosidic bonds. It is secreted by the Aureobasidium pullulans consist of α glucan which is not hygroscopic, nontoxic, odourless, soluble in water, and like other glucans, it is edible. It can form films and has got typical rheological properties due to which it has got wide range of applications in food, agriculture, textile industry, cosmetic and pharmaceutical. It's

commonly found as a mouth freshener or as oral hygiene product [68, 69]. The structure of pullulan consists of three glucose residues held together as a linear polymer. This biopolymer exhibit elasticity phenomenon and also can be used as a flocculating agent for the extraction of mineral oils like potash, uranium and ferric hydroxide. It can be used as a low-calorie food or drink. In biomedicine it can be used as a plasma expander, drug vehicle [75, 77, 78]. Scleroglucan consists of β glucan unlike pullulan and it is a homopolymer. It is extracted from the *Sclerotium* species [79]. It is soluble in water and stable over a wide range of temperature, pH, saline conditions. These properties make it suitable for different biotechnological and medical applications. It is widely used in oil recovery, food, cosmetics and pharmaceuticals [70].

3.1.3 Exopolysaccharides (EPS)

EPS layer is regarded to be having potential activity and possess' remarkable biological activity. Some of them have antioxidant, antitumor, anti inflammatory and are modifiers of immunity [80]. They own resources which can be exploited for modifying the texture, as stabilizers, emulsifiers etc. and also can be useful in medical and food industry [81]. They have got remarkable application in the agriculture sector as they can protect the cell against biofilms and aggregate of cell formation hence used as biofertilizer, for bioremediation of soil, water, for protection of plants, waste water treatment and soil treatment. Studies also suggest that they have got herbicidal activity [62]. The EPS also provides antimicrobial activity [82].

3.1.4 Chitin and Chitosan

Chitin is a polymer that is fibrous in nature and is a major constituent of arthropods and fungal cell wall. It consist of β -1,4-linked N-acetyl-D-glucosamine (GlcNAc). It is isolated from the Ascomycetes, Basidiomycetes, and Phycomycetes species of fungi [60]. Chitin in fungi is found as aminoglucosides in free form and also found bound by covalent bonds to beta glucans [83]. Chitin on deacetylation gives chitosan which is biodegradable, has compatibility, non toxic and is involved in transport of substances hence used as an emulsifier. Chitosan is also employed for the regulated release of the active substances in the food industry, agriculture to prevent contamination by bacteria, viruses and fungi [84]. Some of the other important applications of chitosan include plant protection and resistant induction, as flocculant in the wastewater treatment, oral mouth washes, as anti tumors and in wound healing. Example of the fungi that produces chitosan are *A.niger* and *Mucor javanicus* [85, 86].

3.2 Glycolipids

Glycolipids consist of both carbohydrate moiety and fatty acid molecules attached to it. This complex structural diversity reduces the interfacial and surface tension. Rhamnolipids, trehalolipids, mannosylerythritol lipids, sophorolipids and cellobiose are some of the examples found as a part of glycolipids. They have potential use as biopesticide in agriculture, as emulsifiers, bacteriocidal activities, as a food preservative, as a biosurfactant [87]. They are secreted by the Ascomycota and Basidiomycota. One example of the fungi is *Absidia corymbifera* of zygomycota while *Ustilgo maydis* is another species that secretes larges quantities of the glycolipids consisting of mannosylerythritol and cellobiose lipids [88, 89].

3.3 Lipopeptides

These consist of the fatty acid linked to the amino acids of peptides. The lipid group is hydrophobic whereas the amino acid region confers the hydrophillc region which is usually a linear or a lactone ring. Hence, sometimes found as cyclic molecules if it has lactone confirmation in the hydrophilic region. These biopolymer have got tremendous applications in environmental, medical fields [90]. They exhibit antifungal property to species like *Candida* sp., *Pneumocystis carinii* and some *Aspergillus* sp [91] (Fig. 5).

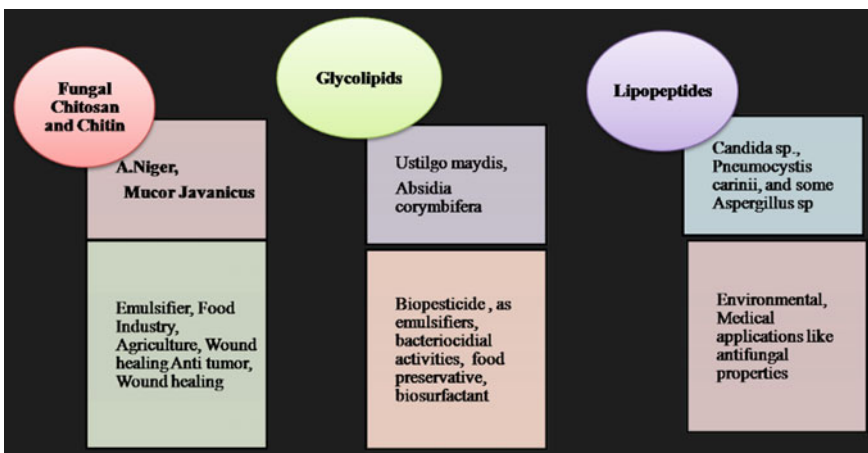


Fig. 5 Sources and applications of Chitosan, chitin, Glycolipids, Lipopeptides

4 Algal Biopolymers

Algae forms another important source for the extraction of biopolymers that are low cost and sustainable. The products of algae are environment friendly. The growth of algae can be possible even in wastewater; it is not dependent only on fresh water. Biopolymers of algae have good application in food packaging, medicine, cosmetics and in pharmaceutical sectors. The biochemistry of biopolymers from algae include polysaccharides, proteins, fats (oils), and others. Algae are dominated by starch and other cellulose polymers [92–94]. These are considered as the photosynthetic machinery that aid in the synthesis of several polymers [95]. These biopolymers from algae are not harmful and has other properties like anti microbial, antioxidant, antitumor and also as modulators of immunity. They also possess strong adhesion properties and tensile strength [96–98].

4.1 Polyesters

4.1.1 Poly Hydroxy Alkanoates (PHA)

These have properties that are similar to the petrochemicals, hence the biopolymers can be a possible substitute to synthetic polymers [99]. Some of the examples of the algae include *Synechococcus subsalsus* *Spirulina*, which produce a 14-18C PHA. The secretion of polymers in them is due to nitrogen deficiency. Their chemical compositions also varies with strain of algae [100].

4.1.2 Poly Hydroxy Butarate (PHB)

They possess properties similar to polypropylene and own properties like optically activity and are non polar. Cassuriaga et al. [99] suggested that when the cell growth rate is not optimum, it leads to accumulation of lipids that are required for biopolymer synthesis. *Chorella fusca* is an example of the Microalage that produces PHB [99, 101]. Studies suggest that the algal biomass when contains high starch amounts bring about the formation of PHB [102]. *Botryococcus braunii* is another example which can synthesize the PHB. The amount isolated from it accounts to around 17.4% as explained by Kavitha et al. [103].

4.1.3 Poly (3-Hydroxybutyrate-Co-3-Hydroxyvalerate) (PHBV)

PHBV is formed from PHB by the addition of hydroxyvalerate into the structure. This results in enhanced properties like decreased degradation rate, making it more reliable tool in the drug delivery [104]. Akdogan and Celik [105] studied the production

characteristics of PHBV using glucose without the need for the extra precursors. The polyesters from algae possess properties like biocompatibility, biodegradability and has biomedical applications in cartilage, bone and nerve tissue regeneration [106].

4.2 Polysaccharides

Poly lactide or polylactic acids are polymers that contribute majorly to the biomedical field. They have been widely used in the manufacture of needle used in the stitching of wound or surgeries, screws in orthopaedic attachments, braces, bandages etc. They also provide biomaterial for the tissue regeneration, wound dressing, augmentation of tissue [107]. Other saccharides include alginates, fucoidans, carrageenan, porphyrin, galactans, ulvans and glucans. These depending on their composition and complexity have varied applications in tissue engineering, cosmetics and cosmetic surgery [108]. Alginates can be extracted from the species *Undaria pinnatifida*. It is used for drug delivery and tissue engineering. They on binding to cations can form hydrogels and has excellent water retention capacity and improved adsorption properties [109]. They also have been used as a tool in biorefinery [110]. Fucoidan with its heterogenous structure finds its importance in the treatment of cancer due to the high sulphur content of the sugar residue and is also employed in pharmaceutical industry. They are isolated from brown algae [111–113]. The fucoidan from *F. evanescens* is low in its molecular weight, high in sulphur content comprising around 96% of monosaccharide residues in the structure and shows properties like antitumor activity and inhibits neutrophil migration [114]. Laminarian is a non-hydrocolloid polysaccharide containing glucose residues e.g. *Laminaria hyperborea* [115]. Some of its widespread applications are in aquatic carbon cycle, production of ethanol, drug delivery, antitumor, antioxidant, anti-inflammatory [116]. Carrageenan is extracted from red seaweed, *K. alvarezii*, *Eucheuma spinosum* [117]. Its applications includes high gel strength, high viscosity, drug delivery [118].

4.3 Polyalcohols

These contain properties like increased tensile strength which are easily degradable and soluble in water. Polyvinylalcohol is one of the mostly used among polyalcohols. It is used as emulsifier, as protective films and agents for sizing. Using algae as a filler material has also been studied. The algae and the polyvinylalcohol composition is shown to increase the mechanical properties like thermal stability [119] (Table 3).

Table 3 Biopolymers from algae

S.no	Name of the biopolymer	Name of the algae	Application	References
1	N ₂ deficient PHA (Polyester)	<i>Synechococcus subsalsus</i> , <i>Spirulina</i>	Biomedical applications like cartilage, bone and nerve tissue regeneration	[100]
2	PHA that are not N ₂ deficient (Polyester)	<i>Chlorella minutissima</i>	Biomedical applications like cartilage, bone and nerve tissue regeneration	[100]
3	Polyhydroxybutarate (Polyesters)	<i>Chorella fusca</i> <i>Botryococcus braunii</i>	Optically active	[99, 101, 103]
4	Alginates (Polysaccharides)	<i>Undaria pinnatifida</i>	Drug delivery and tissue engineering	[108]
5	Fucoidan (Polysaccharide)	<i>F. evanescens</i>	Anticancer activity, antitumor activity inhibits neutrophil migration	[114]
6	Carrageenan (Polysaccharide)	<i>K. alvarezii</i> , <i>Eucheuma spinosum</i>	High gel strength, high viscosity, drug delivery	[117]
7	Laaminaria (Polysaccharide)	<i>Laminaria hyperborea</i>	Aquatic carbon cycle, production of ethanol and drug delivery, antitumor, antioxidant, anti-inflammatory	[116]

5 Conclusion

The biodegradable polymers or the polymers produced by various microbial flora has occupied greater value and place in many fields and is being used in the manufacture of many commercial products. It is another rapidly developing area that is grabbing the attention of scientists and from industry. It is understood that it has got a huge potential and there are some areas which still need focus. It is also offering solutions to environmental issues. Challenges associated are optimization of the production on a large scale from identification of strain, validation of the protocol and purification of extracted biopolymer. With the help of present biotechnological advancements and inter disciplinary approach, the optimization process can be made more feasible.

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The Scope of Biopolymers in Food Industry



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Abstract Biopolymers are natural macromolecules that can be utilized for the fabrication of eco-friendly products with the goal of sustainable development. They are highly biocompatible, environmentally benign, and starting reagents/modifiers in many reactions. The physical and mechanical properties of biomacromolecules/polymers are not up to the mark for direct industrial applications, especially in packaging and product formulations. So they are supposed to undergo a certain degree of modifications or new innovative routes are devised to formulate value-added industrial-grade biopolymers. Mostly, additional co-polymeric units, clay, nanomaterials, and other additives (crosslinkers or initiators) are incorporated during the fabrication process. The available functional groups, modifiable hydrocarbon chains, and unsaturated units make these biomacromolecules or polymers make them one of the reactive reactants or suitable backbones in various polymeric chains for different applications. The surpassing utilization of biopolymers in the biomedical and food packaging industry makes them phenomenal as well as a prime topic in the R&D sector. Also, they play a key role in lowering the overall carbon footprint, particularly in the packaging industry. Due to the global population demands and adverse environmental effects of petrochemicals, biopolymers have gained much attention in every alternate industry, but far more notable in food industries for producing value-added products with commercial importance. They are generally considered to be safe (GRAS) with appropriate appearance, texture, taste, and smell. Further, the nutritional and sensory values of the products can be

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tuned based on the decided application of the material. Biodegradability gives significant value to all biopolymer-based products for direct human application (in vivo or in vitro). The application in the sector of drug delivery and food sector generates international demand for such polymers. The biopolymers can improve consumers' expectations, experiences, and simultaneously help in maintaining an ecological balance. This chapter highlights various applications of renewable biopolymers in the food industry. The most relevant biopolymers with high potential in food packaging, food design, functional food ingredient, encapsulation, and food manufacturing have been discussed. Moreover, the information related to the source of biopolymer, types, applications, and future potential in the food industry altogether would provide a better outlook.

Keywords Food packaging · Biopolymers · Fabrication · Carbon-footprint

1 Introduction

The polymer industry has a huge turnover and is influencing our everyday life. We are becoming dependent on polymers, and most of them are fabricated from petrochemicals, thereby causing harm to the environment. So, there is a big demand for the substitution of petro-based polymers by biopolymers. Biopolymers are natural macromolecules and are mostly produced from living organisms or their by-products. Biopolymers such as cellulose, starch, polyhydroxyalkanoates (PHA), chitosan, alginate, gelatin, and many others are abundantly available in the free or conjugated form in nature. They may have repeating units of sugars and amino acids or aliphatic polyesters, unsaturated hydrocarbons, and various other function moieties. The overall molecular weights rely on the repeating units, route of synthesis, co-polymerizing units, and other subsequent modifications.

Polymers can broadly be classified into different scales: (i) Biodegradable or non-biodegradable, (ii) Polymeric backbone units, (iii) Repeating units, (iv) Natural or synthetic, (v) Plastic or elastic polymers, and others. All these variations can alter the properties of any polymeric unit. Based on the possible utility, particular polymers with certain functional groups are prepared and employed in different applications [51]. Functional units of vinyl, polyamide, polysaccharides, polycarbonates, or polyesters can be generated or incorporated in the backbones of the polymer would impart special abilities such as hydrophobic strength, refractive index, biodegradability, hydrolytic stability, and others [52]. The arrangement of the functional groups and repeating units generally defines the overall chemistry of the polymer. The formulation of the end product and its properties can be easily tuned or determined by studying the arrangement of functional units. For example, the function of nucleic acid depends on the sequence of nucleotide units, properties of polysaccharides are affected by sugar units and type of linkages, whereas the ability of proteins is decided by amino acid units. Based on the end groups and associated functional units

biopolymers can also be utilized as biosurfactants, bio-fluctuant, bioplastics, degradable coatings/films, etc. [117, 142]. The processing routes involved like natural, green chemistry, microorganisms, or others, are also a very important basis during classification and can influence the application of biopolymers in various industries [79, 80, 98]. Direct biomass-based polymers, biomass-derived monomers, and oil-based synthetic polymers [61] have varied applications ranging from food packaging, encapsulation, edible films, and coatings. In the food industry, biomass-based materials such as proteins, polysaccharides, and lipids are responsible for gas and aroma barriers. They also have high rigidity and very strong water sensitivity due to their hydrophilic nature [40]. In food packaging, the use of proteins and polysaccharides would enhance the gas barrier properties and control the water sensitivity of the product. Proteins, polysaccharides, and lipids are nowadays used in edible films and coatings for moisture loss restriction, gas permeability control and microbial activity control, and product structural integrity preservation. Natural compounds are responsible for expanding the shelf life of food and increasing its preservation by protecting them from oxidation and microbial spoilage. A food coating out of such biopolymer based active molecules would generally be used by marketing, packaging, and product delivery industry to extend the shelf life of the product [41]. Researchers looked at the impact of edible coatings on the consistency of frozen fish fillets. Fillets were coated and stored for up to 7 months at 18 °C. According to the findings, the coating layers on the surface of the meat offered greater resistance to mass transfer during storage [36]. On the other hand, synthetic petrochemical-based films have high physicomechanical stability but are non-biodegradable and cause environmental harm [100, 110].

Nowadays, the fabrication of biopolymers by mimicking natural pathways is most favored, few examples in this direction are polymers fabricated by mimicking spider web, hydrophobic lotus surface, and biodegradable natural materials. Biopolymers drafted from animals, microorganisms, agricultural feedstock, marine, and algae are also mostly explored in the food industry. As through animal sources, collagen and gelatin are produced, marine source produces chitin as the major product which is processed into chitosan. Microbial metabolites produce lactic acid that transforms into Polylactic acid, Agricultural feedstock produce biopolymers such as carbohydrates, lipids, and fats which can be converted through chemical synthesis or by microorganisms [92]. Other sources like microorganisms also play an essential role in producing different kinds of biopolymers like polyamides and polyesters which are used to form plastics. In medical applications like tissue engineering and drug delivery, different types of biopolymers are synthesized [92]. Organic plastics are obtained from various kinds of sources such as pea starch, vegetable oil, and corn starch. Algae are an excellent source for plastic production due to their high yield and ability to grow in habitual conditions. So, based on the source and properties the biopolymers are utilized in variety of industry as stipulated in Fig. 1.

In 2018 [57] biopolymers have played an important role in the food industry and more insight has been put forward to utilize them in improving the physico-chemical properties of foods. Production of food naturally is more sophisticated in a contemporary manner, and the overall protein or vitamin content in processed

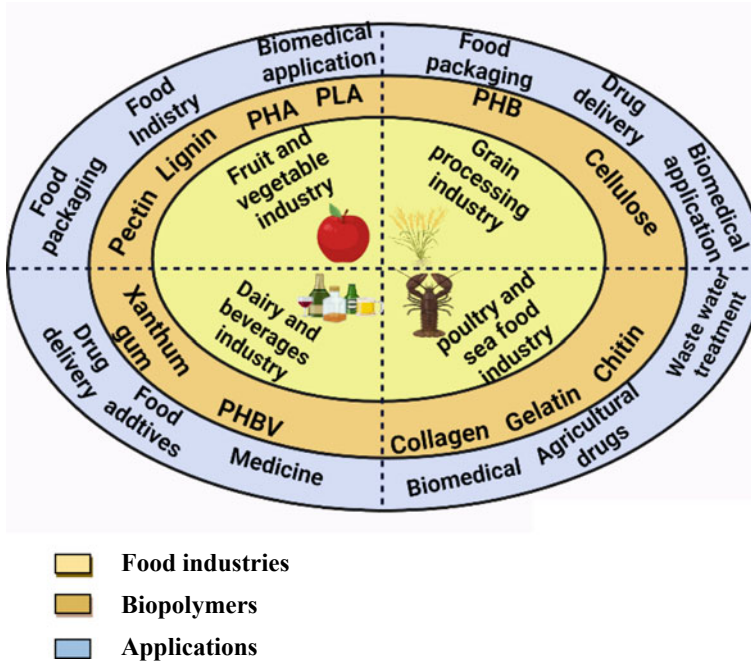


Fig. 1 Chart representing the source, biopolymers obtained, and potential applications in food and other industries

foods is constantly decreasing. So, the bioactive compounds have great potential with many health benefits which can preserve the value-added properties of any food material. They act to improve the stability of certain bioactive compounds like probiotics, polyphenols, minerals, phytosterols which are highly reactive to light, water, O₂ and heat, vitamins, omega-3 fatty acids, etc. However, the bioactive compounds are more stable only under critical parameters in various food systems [34]. As a solution, biopolymers are used for encapsulation of these bio-actives using different chemical methods including cocrystallization, molecular inclusion, interfacial polymerization, and mechanical methods including spray drying, spray chilling, extrusion, and fluidized bed [37]. Biopolymers like hydrocolloids act as food additives in several recipes. Specific roles performed by them are film-forming, stabilizing, thickening, gelling, and encapsulating agents. Based on the molecular behavior, chemical reactivity, and molecular weight they are readily investigated in the drug industry [10].

The chemical structures of the monomeric unit during polymer preparation have a great role in the effective properties of the material [49]. Thermal stability, flexibility, good barrier to gases, water, resistance to chemicals, biocompatibility, biodegradability, and many other properties can be tuned by creating variation in the structural backbone of the polymer required for different areas of work. With the increase in demand of consumers, renewable sources are the most preferred source to prepare

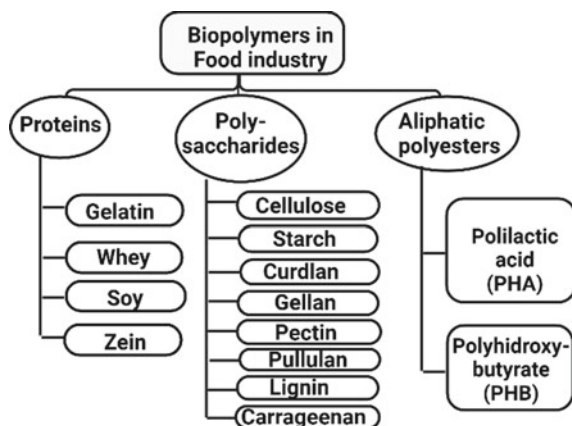
products and reduce overall wastage [118]. Synthetic polymers are mostly used due to the ease of handling, mechanical strength, and cost-effectiveness of such materials. However, it is observed that in all sectors of the economy, biopolymers are found to be versatile, environmentally friendly and can be generated from different biowastes like wing feathers of dead animals, hair, bones, vegetable seeds, oils, stems, etc., for different applications [102]. The understanding of biopolymers based on their functionalities, source, and application would further improve the quality of research in the present scenario. Further on demand of environmental sustainability and economy, synthetic agents are constantly tried to be replaced by natural and biodegradable agents.

2 Most Important Biopolymers in the Food Industry

Today, consumers are health cautious and demand the manufacturing of environmentally benign materials. These biopolymers are derived from three groups [40] (i) Biomass-based polymers (Polysaccharides and Proteins), (ii) Synthetic biopolymers (PLA and PHB), and (iii) Natural biopolymers (Bacterial cellulose and PHA).

With technological and scientific advancements many biopolymers have been used for the commercial application of food packing. For an instance, biodegradable polyesters (starch, Polyhydroxyalkanoates (PHA) and Polylactic acid (PLA)) are commercially available which are used in different sustainable monolayer and multilayer packaging applications [8]. Similarly, a few of the polymers and their utility in the food industry have been highlighted in Fig. 2. Several studies on the application of coatings to minimally processed or fresh-cut fruits and vegetables have also been published. Furthermore, coatings may be used to add flavor or nutrients to food.

Fig. 2 Types of biopolymers used to make edible products such as proteins, polysaccharides, and aliphatic polyesters



2.1 Proteins

2.1.1 Gelatin

Gelatin is a protein present in bones and skin, which can be extracted by hydrolyzing collagen [66]. The source of gelatin is collagen I, and it can be produced basically in two forms Type A and Type B, based on its synthesis, procedure, and composition. Type A is produced by acid hydrolysis of collagen, and Type B is produced by alkaline hydrolysis of collagen [9]. The chemical structure of gelatin contains a large number of glycine, proline, and 4-hydroxy proline residues [29]. It can be modified with biomolecules and nanoparticles due to the functional groups like $-NH_2$, $-SH$, and $-COOH$ for a wide number of applications [83]. It is used for the preparation of candy, marshmallows, or desserts. The demand for gelatin is increasing worldwide for making chewy candies, so-called gummy candies [81]. Porcine and bovine are the polymers found in mammals that are most commonly used biopolymers. According to the previous studies, the various food applications, for gelatin, have increased because of biodegradability, zero toxicity, and gelling ability. They have been mostly used biodegradable films, emulsifiers, foaming agents, and stabilizers [54, 66].

2.1.2 Whey Protein

Whey protein is the by-product, obtained from cheese production, which contains the protein isolate (WPI). The structure of whey protein contains a group of globular proteins that are highly structured including primary, secondary, tertiary, and also quaternary structures [135]. Whey protein is gaining the attention of researchers due to its functionalities such as gelation, foaming, emulsification, solubility, and thermal properties. It is used to improve the food's sensory quality and enhance the texture [68]. It acts as a good fat replacer and texturing agent for yogurt. It can stabilize emulsions and improve the overall texture when added to whole fat yogurt prepared from skim milk powder [69]. Whey protein has properties of good oxygen barrier and moderate moisture permeability which is beneficial for the packaging [99, 136] forming elastic films.

2.1.3 Soy Protein

Soy Protein is also known as soybean protein, and they are found in various forms such as soy flour (SF), soy protein isolate (SPI), and soy protein concentrate (SPC) [53]. The main property of soy protein is that it is useful in the food industry as an emulsification and texturizing agent [134]. The manufacturing function of soy protein is used to form plastics [130], adhesives, and packaging materials as an environmentally benign alternative to petroleum polymers. The functional properties of proteins are the physicochemical properties that influence the behavior of proteins

in food systems, with regard to food preparation, processing, and storage. These properties are an important means of determining the quality of the final product and facilitating its processing [91]. In general, soy protein possesses great potential for enhancing many processing properties, such as emulsification, gelation, foaming, and water, and fat absorption, all widely accepted attributes of food.

2.1.4 Zein

Zein is a naturally occurring protein-polymer obtained from the corn (*Zea mays* L.) during industrial corn processing which is used to develop different kinds of thermoplastic products [104]. The structure of the Zein protein contains high content of non-polar amino acids due to which it has a hydrophobic nature [94] and also has the advantage of an excellent barrier to oxygen but lead to the worst mechanical properties.

2.2 Polysaccharides

2.2.1 Cellulose

Cellulose is the biopolymer present in the plants and bacteria as a reinforcement material [96]. Cellulose is a polymer of β -D-glucose. The chain units are linked by β -(1 \rightarrow 4)-glycosidic bonds. In cellulose the groups $-\text{CH}_2\text{OH}$ are oriented alternating above and below the plane, thus producing long linear chains [143]. Cellulose is insoluble in water and other ordinary solvents; however, the hydroxyl groups of cellulose can partially or completely react with various reagents to produce derivatives with properties desired and/or required for food applications, namely, in terms of solubility [143]. Bacterial cellulose is produced by *Sarcina* and *Agrobacterium* [17]. Nowadays cellulose is extracted from brown alga *Laminaria*, green algae such as *Valonia*, *Halicystis*, and *Cladophora* [116]. Cellulose has high hydrophilic property [45] and has unique structural as well as mechanical properties.

2.2.2 Starch

Starch is a hydrocolloid biopolymer and hydrophilic which is reproduced by plants in a granular form of different sizes within the endosperm. The essential sources of starch are wheat, rice, and potatoes. Starch is a biopolymer which easily commercially available and most biodegradable material, and it happens due to its balanced properties (e.g., through companies such as Novamont and Natureworks, respectively), being produced on a large industrial scale. It has the great property of giving texture to many foods and is widely used in food and industrial applications [41]

acting as a water retention agent, thickener, bulking agent, colloidal stabilizer, and gelling agent.

2.2.3 Curdlan

Curdlan is produced by *Alcaligenes faecalis* var. *myxogenes*, and *Agrobacterium* sp. Curdlan biopolymer is insoluble in water and contains heat gelling [140] and water binding properties which are beneficial for the food. Curdlan is a linear polymer composition from β -1,3-glucan. The basic unit of Curdlan is glucose with high molecular weight. The chemical formula of Curdlan is $(C_6H_{10}O_5)_n$. The current applications of Curdlan in the food and biomedical industries are stated as being used in milk and dairy products, meat products, noodles, tofu, probiotics, etc. [133].

2.2.4 Gellan

Gellan is a linear anionic heteropolysaccharide having tetrasaccharide repeating units and has the capability for partial or total replacement of existing gelling agents [19, 108, 126] which is extracted from the *Sphingomonas elodea* bacterium also named as *pseudomonas elodea*.

2.2.5 Pectin

Pectin is a water-soluble biopolymer mostly found in the higher plants with the major structure consisting of linear chain regions [46]. Pectin is functionalized in different industries as a colloidal stabilizer, thickening, and gelling agent, texturizer, and emulsifier [121]. It is also used as a biomedical product in cancer treatment [44].

2.2.6 Pullulan

Pullulan is a water soluble biopolymer and non-ionic polysaccharide but insoluble in organic non-water- miscible solvent. *Aureobasidium pullulans*: this type of fungus is the major source of this biopolymer [32]. Nowadays this biopolymer has a huge variety of applications [24] such as in medicine, cosmetics, food, and ecology with different purposes like remediation agents, flocculants, blood plasma substitutes, and additives.

2.2.7 Lignin

Lignin is a biopolymer produced from wood to obtain pulp. Lignin binds with polysaccharides such as cellulose and hemicellulose. Lignin can be extracted from

different types of biomass [23]. It has a unique chemical structure than other biopolymers such as cellulose and chitin due to the absence of glucose residues that are replaced by aromatic heteropolymers. It is a redox polymer formed of aryl propane structural units. The chemical structure of lignin is based on the three subunits as trans-coniferyl alcohol (G), trans-sinapyl alcohol (S), and trans-p-coumaryl alcohol (H) [42]. Lignin yield is affected by various parameters such as reaction time, method of extraction, temperature, and type of reaction medium. Studies of lignin are related to herbaceous plants and partly aim to digestibility and dietary conversion issues in animal feed [28]. Recently the main challenge is to make lignin-based products suitable for commercial use because of their complex structure [106]. According to a recent study [119] ethers are synthesized from lignin through suitable chemical reactions.

2.2.8 Chitosan

Chitosan is a biopolymer of amino polysaccharides and derivatives obtained from chitin. They have been used in different fields of research such as material science, biotechnology, and other fields [43]. Properties of chitosan include biocide properties and antimicrobial properties such as against viruses, bacteria, and fungi [31]. Chitosan can be obtained from wastes obtained from the shellfish industry and for this reason, is an abundant material. It can be obtained from the chitin component of fungal cell walls (*Aspergillus fumigates*, *Histoplasma farciminosum*) and from the yeast *Saccharomyces cerevisiae*, too [82]. The forms of *Mucor rouxii* (filamentous and yeast-like) contain large quantities of chitosan [90, 124]. Chitosan has multiple applications in the food industry [60], agriculture [58, 63, 77, 113], pharmacy [59], medicine [112], cosmetology [65], textile and paper industries [107], and in chemistry [47] because its high nutritional quality.

2.2.9 Alginate

Alginate biopolymer is used in a wide range of industries such as food additives, textile printing paste, paper coating, pharmaceuticals, wound dressing, and many other novel end-use. It also functions as a gelling agent, thickening agent, and colloidal stabilizer. Brown algae such as *Laminaria* and *Macrocystis* are major sources of the alginate biopolymer [126]. The structure of the alginate contains the carboxyl group in each constituent residue, and it is a binary copolymer of (1–4) glycosidically linked β -D-mannuronic acid and α -L-glucuronic acid monomers [49].

2.2.10 Carrageenan

Carrageenan is a type of polysaccharide used in the food industry obtained from the red sea wood, mainly K-carrageenan [20]. This biopolymer mainly has three

dominant species as (Kappa) κ , (Iota) ι , and (Lambda) λ -carrageenan. Potential applications expand to other industries which include pharmaceutical, cosmetics, printing, and textiles. The application of carrageenan in the food industry is as a milk stabilizer, gelling agent, meat and poultry, toothpastes, pet food, air freshener gels, immobilized cells, and biocatalysts, and neuroprotective [93].

2.2.11 β -Glucan

Glucan is a dietary fiber component of food that can be extracted from bacteria, oat, yeast, and barley. It has several physiological effects, such as reducing plasma cholesterol levels, controlling postprandial glucose levels, and modulating the immunological system [5]. Its chemical structure contains a non-starch polysaccharide that belongs to the carbohydrate family and also contains long chains of glucose that can be branched or unbranched. Scientists have enlightened the new sources of research advances [4]. Generally, cereal has been the most common source of β -glucan extraction, or these sources have been used in an unpurified form in the production of food items. Currently, the new sources of β -glucan are marine animals, mushrooms, algae, yeast, bacteria, and molds [2]. Other plant sources which have a minor amount of β -glucan are millet (*Panicum miliaceum*), beans, corn/maize (*Zea mays*), flax, canary seed (*Tropaeolum peregrinum*), lentil (*Lens culinaris*), peas, spelt (*Triticum spelta*), spring wheat, and winter wheat [5]. β -glucan is promising alternative for food product development with nutraceutical status because of its documented health advantages. It is used in bakery products, dairy products, meat products has been the subject of research during the last decade. About industrially relevant qualities of these items, there is still room to explore further avenues for product development.

2.3 *Aliphatic Polyesters*

2.3.1 Poly(lactic Acid) (PLA)

PLA or Poly(lactic acid) is a biodegradable polymer and agricultural product. They can be obtained from sugarcane, corn, and other sources [12]. It is produced by starch fermentation from lactic acid. PLA is formed from lactic acid through lactic bacteria via starch fermentation. Almost all of the lactic acid generated by this biotechnological approach is L-lactic acid [137]. PLA has excellent mechanical properties [134]. It is a hard material similar to acrylic plastic which is insoluble in water, and it is completely decomposed under compost conditions such as under microorganisms and marine environments. The stiffness of this biopolymer can be reduced by the addition of plasticizers, but it also reduces the transparency and oxygen barrier properties [131]. In the recent era, PLA biopolymers produce a great interest in the packaging industry and earth-friendly biodegradability. PLA has the properties such

as resistance to oil-based products, flavor or odor barriers to foodstuff, and sealability to lower temperature [109]. Properties like good water resistance and excellent oxygen barrier give interest to the food packaging [40]. The main drawbacks of these polymers are excessive brittleness and insufficient barrier to oxygen [131] and water and also have a low thermal resistance.

2.3.2 Polyhydroxybutyrate (PHB)

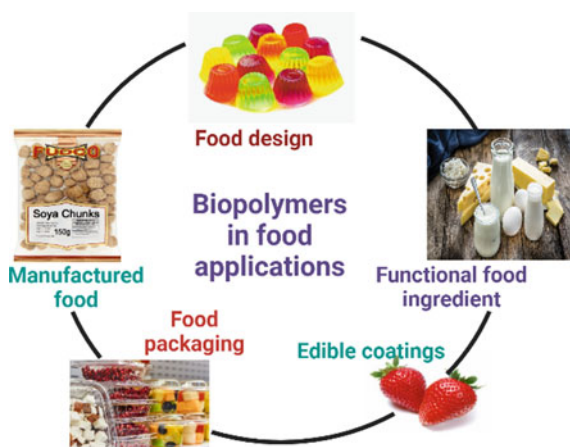
PHB is a naturally occurring biopolymer and biodegradable PHA (Polyhydroxyalkanoates) [48]. *Ralstonia eutropha* is the most widely studied bacterium that accumulates the PHB in large quantity [67]. The general structure of PHB can vary due to the distinct type of bacteria and the feed used to develop PHB. Typically $-(CH_2)_n-CH_3$ is the most naturally occurring PHAs [22]. Most recent application of this biopolymer includes medicine, pharmacy, agriculture, packaging industry, and food industry.

3 Functional Biopolymers in Food Manufacturing and Food Designing

3.1 Edible Films and Coatings

Polymers can shape thin films when they are processed in a specific way. These films can be desirable for certain uses, ranging from drug delivery to food products. Solvent evaporation, also known as solvent casting, is a popular method of film-forming and manufacturing. The fact that these films are edible is the most important criterion in food applications as shown in Fig. 3. Since organic solvents are harmful

Fig. 3 Biopolymers rapidly utilized as food coating, food manufacturing, food packaging, edible coatings, antimicrobial films, dairy products, etc. in food industry to increase the quality of food



to the environment and human health, water-based solvents or listed safe organic solvents are preferred. Biopolymers are the most visible ingredients for edible films. The disintegration rate, taste, and mechanical properties of the resulting film are all influenced by the biopolymer used. Some foods may be coated with these films to shield them from environmental factors such as oxygen, nitrogen, and humidity. They can also be found as stand-alone edible films with a specific food ingredient or scent. The film ingredients and processing conditions should be optimized depending on the required time of endurance on the coated product or when it has to be eaten [85]. A variety of biopolymers may be used as coatings or in the making of edible films. Chitosan is a type of linear polysaccharide that is often used in these types of applications [141]. Coating foods with chitosan films in the food industry can slow the oxidation of phenolics and prevent browning. Because of its antimicrobial properties, it also helps to reduce microbial development. When mango is sliced, the color and taste shift quickly. The use of chitosan-based edible film to coat mango slices extends the shelf life and improves the consistency of the slices. Olives are high in fatty acids and phenolics, all of which are good for human health. The nutritional value of olives decreases throughout maturation and storage due to the oxidation of fatty acids and polyphenols with antioxidant ability. The nutritional value of olives was preserved by coating them with chitosan film, which significantly reduced the oxidation rate. Hydrocolloids are commonly used as food additives in a variety of foods.

Globally, nearly 5 million tonnes of plasticizers with about 60 polymers and more than 30 product groups were manufactured annually over the last decade [14]. Plasticizers are non-volatile, low-molecular-weight additives used in the polymer industry to increase the flexibility and processability of polymers [103]. However, in recent years, regulations and health-related concerns have prompted toxic plasticizers to be replaced with biodegradable biopolymers. Plasticizers are used to solve the brittleness and fragility issues that biopolymers have. Natural biodegradable plasticizers, which have low toxicity and good compatibility with a variety of plastics, resins, rubber, and elastomers, have attracted the industry, as has a growing global trend for the use of biopolymers [33]. By shielding food from moisture, heat, gases, solvents, insect, and microbial attacks, packaging films or coatings play an important role in extending shelf life. As antibacterial agents, biodegradable polymers such as Polylactic acid (PLA) and Polycaprolactone (PCL), lemon extract, thymol, and lysozyme were used to create packaging material. The pathogenic material regulates the oxidation and moisture migration rates of fresh fruits and vegetables, which is beneficial because oxygen triggers off-odor and off-flavor; unwanted color changes, and decreased nutritional quality of the food due to oxidation changes. Biodegradable packaging made of biological materials has several benefits over plastic packaging [6]. The antimicrobial properties of chitosan-based packaging material make it a good choice for pathogenic and spoilage microorganisms. Biopolymers have been used as a coating to minimize oil absorption during deep oil/fat frying of foods for the past two decades. Deep fat frying is used to make fried foods like potato chips, extruded snacks, fish sticks, fried chicken, and batters. Since people are aware of the connection between saturated fat and coronary heart disease, refined oil intake has

increased. Biopolymer is now being used as a coating in different food forms to introduce low-fat products. To minimize fat content in fried foods, alginate, powdered cellulose, soy protein, and Gellan gum were used [11]. Biopolymer coatings may be made of protein, carbohydrates, or lipids, and they may act as a moisture or gas barrier to help fresh or minimally processed foods last longer. They observed changes in weight, firmness, soluble solid concentration, decay percentage, and color production in fruits after applying gum arabic as a coating to green mature tomatoes, using non-coated fruit as a control; 10% gum arabic was delayed to uncoated control fruit. Furthermore, edible coatings of water-soluble chitosan, acid-soluble chitosan-carrageenan, and sodium alginate were used on fruits at 20 °C for up to 15 days. In comparison to commercial shellac coatings, Zein coatings are applied by dissolving 10% Zein solution in 10% aqueous alcohol and display good fruit consistency.

4 Industrial Utilization and Processibility of Biopolymers

Renewable biopolymers gained the attention of food industries for producing value-added food products of commercial importance. The biodegradability of biopolymers allows them to be used in a variety of applications. Production of edible and biodegradable materials for the food industry is based on the specific characteristics of the polymeric material and applicational prospects. Edible films and coating are used to protect confectionery products, seafood, fruits and vegetables, canned, meat, and frozen products which largely reduces the waste as well as possible contamination of synthetic organic molecules [56].

4.1 Freeze Drying of Fruit and Pulp Processing

Food products stored for long-term usage require specific temperatures, pressures, and phase changes (liquid gel or liquid–solid). These developments affect food quality and stability due to the changes in physical properties of foods while phase transition [86]. Crispy items lose their crunchiness in rubber sheaths, resulting in solute crystallinity in food powders. New products are being developed to encourage fruit consumption by improving sensory, nutritional, and functional quality requirements. As a result, dehydration or frozen fruits, as well as extracts or juices derived from fruits or powdered plants, are used in the pharmaceutical and food industries to produce a wide range of fruit products [129]. Major problems associated with fruits and freeze-dried pulp are a drastic degree of porosity, decreased aroma retention, lower rehydration capability, and other harmful changes. Many sugar-rich foods, such as coffee and honey, are affected as well, with problems of sticking, cracking, and collapse. Viscosity affected by temperature causes stickiness. When amorphous fruits and pulps were dried at critical temperatures, a series of deteriorating changes were observed. Interparticle bridging induces caking of sticky powders, which results

in a loss of structure and a reduction in sample volume [62]. Orange-juice powder was reported by Shrestha et al. [114] grapefruit by Telis and Martínez-Navarrete [128, 129] and mango, tomato, and pineapple by Jaya and Das [64]. The addition of carbohydrate biopolymer to hygroscopic food powders prevents structural and color changes in fruit powders. Some of these biopolymers are maltodextrins, gum Arabic and some modified starches, fibers, proteins, or inorganic compounds. As a result, biopolymers are known as drying aids or carrier agents. The addition of biopolymer to the fruit pulp or juice is usually done before drying [64]. Maltodextrin is used as a binding agent in finished dried goods to keep their usable properties [26]. Gum arabic is a hetero polysaccharide that is an encapsulating agent. Maltodextrin and gum arabic were used as 0.18 kg/kg pulp for persimmon fruit pulp [13] and Borojia pulp [87]. As a result, carbohydrate biopolymers, mostly gum arabic and Maltodextrin, are used as freeze-drying aids in fruit pulps and juices.

4.2 Food Texture and Gelation

A polymer gel is a three-dimensional cross-linked network that exhibits rheological action that is halfway between liquid and solid. In protein gels, chemical cross-linking completes disordered structures due to denaturation, which enables protein sites to interact via covalent bonds. Thus, the type of structure determines the rheological properties and water-holding of the gels. Gels with large pores and lower density have poor water-holding capacity. A biopolymer that confers semisolid characteristic is used in many food products, including cheeses, sauces, yogurts, sausages, puddings, and other desserts, to give them semisolid properties. Dimensions, surface activities, polarity, thermal stability, and environmental conditions such as temperature, shearing, strain, ionic strength, pH, and macromolecule water activities all influence the structure of biopolymer gels [97]. The disorder of the gel network leads to the creation of fine structures based on covalent and physical bonds, such as Vander Waals forces and hydrogen bonding. The useful parameter in terms of product texture is gel palatability [73]. The extent of chemical functionalization, linkages, and interactions form the different structures of alternative crystallinity. The degree of pectin esterification and alginic acid acidification affects ionic-induced gels made from the respective materials [35]. Curdlan, starch, and collagen shape heat-set gels are a result of conformational structural changes, intermolecular interaction, and water-binding ability [120]. Some protein gels may change their physicochemical properties, such as texture, color, water-holding ability, and microstructures, when modified. Cold-induced gelation, acid-induced gelation, ion-induced gelation, and enzyme-induced gelation are all examples of chemically induced gels. In cold-induced gelation, globular proteins are heated to cause globular structure unfolding and reactive group exposure [138]. According to Kuhn et al. [70] at room temperature, a fine transparent cold-set whey protein isolate (WPI) gel can be made by adding small quantities of salts. The increase of WPI concentration led to a decrease of porosity of the gels and an increase in hardness, elasticity, and water-holding capacity.

4.3 *Biopolymeric Nanomaterials in Food Packaging*

The “oxygen scavenger” was the key packaging technology focused on blending to produce barrier properties until recently. By trapping permeated oxygen from both the headspace and the outside, this technology helps to ensure that relatively low levels of oxygen are in contact with the food as shown in Fig. 3. However, in carbonated drinks, a carbon dioxide barrier is also needed. The majority of industrial plastic packaging products, such as Polyethylene terephthalate (PET) and its main sustainable equivalent PLA are inadequate barriers to these gases. As a result, multilayer structures with one layer forming a high barrier to carbon dioxide and oxygen while the scavenger lowers oxygen levels in the package headspace had to be devised. Since PET nanocomposites are extremely difficult to obtain in a monolayer case due to the high temperature needed to process the polymer, nanocomposites are still manufactured for use in multilayer systems in PET bottles [111]. Food packaging applications in aromatic items, resealable pouches, and dehydrated products, as well as packaging applications in a vacuum and other changed atmospheres, require ultrahigh barrier properties. Non-food-contact approved ammonium salts, such as organophilic chemical modifiers, are used to improve the structural properties of engineering polymers. Only food-contact permitted materials and additives, in amounts below their corresponding threshold migration levels, should be used in food packaging applications. Only the so-called second-generation nanocomposite appears to meet the requirements of current food contact legislation [122]. Nanocomposite formulations are in second-generation that are engineered to meet current requirements, while still being cost-effective and developed to target particular materials (including biopolymers), material properties, or manufacturing technologies. Second-generation nanocomposites are products with precise characteristics rather than standardized formulations with a broad range of applications [25]. Lamellar clays and carbon nanotubes are used in the majority of nanocomposites in plastic applications. Other forms of reinforcing elements, such as biodegradable fibers obtained through electrospinning, are on the other hand, very promising in a variety of application fields.

5 Nanostructured Biopolymers for Improved Food Quality and Safety

5.1 *Antibacterial*

Manufacturers have been encouraged to develop new packaging innovations in response to the growing global demand for minimally processed, easily prepared, and ready-to-eat “fresh” food items [95]. Since it increases shelf life and enhances food protection by scavenging oxygen, moisture, or ethylene and encouraging the emission of ethanol, flavors, and antimicrobial agents, active packaging is a revolutionary way to meet changing consumer demands and industry trends [74]. The food and

packaging industries are paying more attention to antimicrobial packaging because the use of preservative packaging films has many benefits over the direct addition of preservatives to food items [123]. In this context, using engineered nanomaterials to enhance the functionality of biopolymers used in antimicrobial food packaging and antimicrobial food contact surfaces is seen as a promising method [75]. The antimicrobial efficacy of nano-clays and nano-silver, and thus their potential use in active packaging systems has been demonstrated in many of the in-vitro experiments, as summarized by Kuorwel et al. [71]. Metal nanoparticles can also be electrospun into sub-micro- or nanofibers to create masterbatches, which can then be melted, mixed with polymer pellets, or, even better, used as active coatings on polymer surfaces [7]. The electrospinning technique effectively prevents the agglomeration of metal nanoparticles in active food packaging and significantly improves their antimicrobial activity [18]. Aside from metal nanoparticles, electrospinning is being considered as an interesting alternative for active food packaging because it allows for the inclusion of other natural compounds such as essential oils [139]. Cinnamon essential oil, cyclodextrin, and polyvinyl alcohol (PVA) nanofibrous films showed excellent antimicrobial activity against Gram-positive and Gram-negative bacteria in in-vitro studies [88]. Natural polymers like chitosan and cellulose, as well as synthetic polymers, have been used to create nanostructured antimicrobial materials. Chitosan, the original antimicrobial, was used by Torres-Giner et al. [132] for the preparation of active fiber using electro spinning by Cárdenas et al. [16]. A cellulose-derived polymer, methylcellulose, has been used to produce silver nanoparticles with strong antimicrobial activity, as well as good mechanical and barrier properties [76]. Silver nanoparticles' antimicrobial properties are combined with vitamin E antioxidant activity in multifunctional electrospun PLA/AgNP/vitamin E nanofibers [88] which could be useful in the fabrication of active packaging structures for fruits and juices.

5.2 *Antiviral Activity*

Enteric viruses are those human viruses that are primarily transmitted by the fecal, oral route, either by person-to-person contact or by ingestion of contaminated food or water, although they may also be shed in the vomitus. Food may be contaminated by enteric viruses during all stages of the food supply chain, and transmission can occur by consumption of food contaminated during the production process (primary production or during further processing), or contaminated by infected food handlers [55]. In a recent innovative study, an active renewable packaging material with virucidal properties was synthesized by the incorporation of silver ions into polylactide acid films. These films showed strong antiviral activity on feline calicivirus (FCV), a norovirus surrogate, using the Japanese industrial standard (JIS Z 2801) [78]. When films were applied to vegetables, antiviral activity was very much dependent on the food type and temperature. Likewise, Bright et al. [15] evaluated the antiviral activity of active packaging. The antiviral activity of adding grape seed extract (GSE), green tea extract (GTE), or cinnamaldehyde (CNMA) into films has also been reported.

Chitosan edible films incorporated with GTE or GSE [3] showed significant antiviral activity against murine norovirus (MNV).

6 Functional Food Ingredient

Alginate and its many derivatives have a long history of use in foods due to their peculiar thickening, gelling, film-forming, stabilizing, and other general colloidal properties. In instant milk desserts and jellies, bakery filling cream, fruit pies, animal foods, and reformed fruit where thickening is useful; gelling is needed, among other things as shown in Fig. 3 [101]. Alginate strengthens icings by making them less sticky and allowing baked goods to be easily wrapped in plastic wrap. Water-in-oil emulsions, such as mayonnaise and salad dressings, benefit from alginate. Alginate prevents ice crystals from forming during the freezing process, resulting in smooth ice cream. A very small amount of PGA can be added to produce healthy and long-lasting beer foam. When opposed to gelatin jellies, which can be made to weaken and melt at body temperature, edible dessert jellies based on alginate gel do not melt and have a distinct, firmer feel. The binder may be a powder of sodium alginate, calcium carbonate, lactic acid, or calcium lactate. When raw meat is used, a calcium alginate gel is formed, which holds the meat pieces together. This method is commonly used in the production of meats for human consumption, such as chicken nuggets, as well as meatloaves for fresh pet food. Using alginate, proteins like soy protein concentrate, and flavors, similar concepts are used to make shrimp or fish substitutes. Pimento olive fillings are made with pimento pulp and onion rings are made with dried onion powder. Frozen fish can also be preserved with calcium alginate films and coatings [101]. Oily fishes, such as herring and mackerel, have been found to become rancid due to oxidation, even when frozen rapidly. The meat consistency is also increased when beef cuts are coated with calcium alginate films until freezing. The meat juices released during thawing seem to be reabsorbed into the meat, and the coating also aids in bacterial infection protection. If necessary, the calcium alginate coating can be easily extracted by resolving it in sodium polyphosphate.

6.1 *Beta-Glucan in Dairy Products*

Fermented dairy products have a lot of potential for developing efficient β -glucan delivery systems from a variety of sources. Glucono—lactoneglucono- δ -lactone is generated when β -glucans are added to milk or milk products, or dairy-based derived protein gels, during the fermentation process that produces acids and oxidative products of monosaccharides [72]. The addition of glucagel, a commercial product derived from barley [105] that is rich in β -glucan dietary fiber, influences the phase separation phenomenon in skimmed milk.

6.2 *Glucan as Meat Product*

Meat and its derivatives are considered functional foods, but they can also be enhanced with additional functional ingredients. This concept of supplementing meat with dietary fiber, β -glucan, and other nutraceutical ingredients for health benefits beyond essential nutrients would open up new opportunities for the meat industry [115]. Ingestion of β -glucan by poultry, dietary β -glucan has an impact on the consistency of broiler breast meat [84]. Researchers found more moisture-holding ability, increased cooking yield, reduced lightness, and adequate textural parameters of burger patties in an attempt to investigate the effects of β -glucan and inulin as dietary fiber sources for low-fat beef burgers [1]. Other uses for β -glucan and other types of dietary fibers in processed meat include binding, filling, extending, and fat replacement [125], as well as adding a synergistic effect with nutrients, controlling pH, improving emulsion stability, increasing water holding capacity, and expanding sensory parameters.

7 **Biopolymers in Microencapsulation Processes**

The creation of new techniques and formulations is aided by the quest for new, active, and nutritious products. Functional foods, which use natural and active compounds to provide physiological benefits and reduce disease risk, are becoming more popular as a way to improve public health beyond basic nutritional functions through a regular diet. Microencapsulation has been used to stabilize and improve the properties of compounds with high potential, especially for the food industry [50]. As a result, microencapsulation has been applied to a variety of compounds in the food industry, the majority of which are linked to: 19% probiotics, 12% flavors, 10% lipids, 8% antioxidants, 7% vitamins, 7% enzymes, 3% dyes, and 1% stabilizers, among others [39]. In the food industry, each of these compounds plays an important role. For example, one of the most recent food industry innovations is the use of probiotics, which are described by the World Health Organization as “live microorganisms that, when administered in adequate amounts, confer a health benefit on the host” [27]. The probiotics are preserved by microencapsulation, which can be used to improve viability during food processing and also for targeted delivery in the gastrointestinal tract, preventing interaction with the stomach’s severe conditions. Flavors, for example, have a wide range of uses in the food industry, but they are extremely sensitive to ambient or industrial processes. Food flavor loss is very common during the storage process. As a result, microencapsulation is essential to preserve and maintain the flavor in the best possible state for consumption [37]. Incorporating vitamins into food systems can also be a quick and easy way to create new functional foods [21]. For example, vitamins are bioactive compounds; they are physiologically active components that have health benefits in addition to their nutritional function [127]. Vitamins are essential micronutrients that are involved in a variety of biochemical functions

in the human body, but they are not synthesized by it, so they must be obtained from dietary sources [89]. As previously mentioned, biopolymers have piqued the scientific community's interest as matrices for the microencapsulation, immobilization, or controlled release of a variety of active compounds, and have been used in the pharmaceutical, food, biomedical, chemical, and waste-treatment industries due to their inherent advantages (biological properties, high biocompatibility, low toxicity) [38]. Microencapsulation of food compounds with biopolymers may improve their properties [30] and enable the development of fresh, nutritious, and active food products because biopolymers are biocompatible and have numerous biological benefits. The global demand for food products should consider microencapsulated food products.

8 Present Scenario and Future Perspectives

Biopolymers have already been integrated to the food packaging industry, although in initial stages, in order to increase the esthetics of the food packed, which is a deciding factor in the popularity of packed food. Biopolymer based edible films can be integrated to the packaging industry to not only increase the shelf life of packed food but also fortify the food thus increasing the value of the food. Plastic material compounded with natural compounds can also lead to enable easy disposal of the packaging material thereby reducing waste and contributing to the ever rising global issue of waste disposal. Biopolymer based packaging material can be effectively manipulated to suit the specific storage procedure of different food products the reducing the waste generated through spoilage of stored food. Fine-tuned control of the gas permeability and the moisture of the gaseous medium in the packaging can better preserve texture of the food, increasing its market value, especially so for fried products namely chips and snacks. Bioactive packaging can decrease the rate of spoilage of the food by microbial activity with the added benefit of customer reassurance that the food is free from toxification due to its interaction with the plastic, a common packaging material, as well as that developed over time as the food reaches the end of its indicated shelf life.

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Potential Applications of Biopolymers in Fisheries Industry



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Abstract The exponential rise in fish-derived biopolymers in the form of nets, gears, food packaging material, lures and traps has revolutionized the fishing industry in the recent years. The promising usage and emerging market potential of biodegradable films has resulted in the circular economy. This chapter summarizes re-use of fish by-products such as chitin, chitosan, collagen, glycosaminoglycans, and hyaluronic acids in multiple applications. The raw fish-derived biomaterial from skin, scales, fins, and eyeballs has good flexibility, tensile strength, and viscosity; thus, commercially viable as a protective matrix. The fabricated fishery waste is recycled in an ecofriendly way to meet the growing market demand. Additionally, the prominent market players that utilizes fish-derived biopolymer to prepare daily essentials like toiletries, paper bags, food packaging material, bottles, textiles are enlisted. Further, various biopolymer typologies of fishery industry are described in detail based on the source of origin, physical appearance and their significant role in pharmaceutical, cosmeceutical, nutraceutical, nanotechnological, and food applications. However, due to some technological barriers in packaging material like film permeability, porosity, oxidation of lipids, discoloration etc. the bioproducts are still at lab-scale; that need to be addressed to reach industrial-scale. Moreover, the chapter discuss about the sustainable strategies to design fish binders, gill nets, fishing lines, traps

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199

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etc. that should be transparent, fragile, dissolvable to avoid ghost fishing and capable to boost the ecological restoration of aquatic bodies. Finally, it covers the commercial aspect of the seafood industry, where the fishery biopolymer is used as an edible functional food, as a biodegradable preservative with enhanced shelf-life and as a bioadsorbent to remove toxic compounds. Over the last few years, the nanotechnological advancement of biopolymers and their blends have been exploited to treat wastewaters for reuse in seafood processing industry. Therefore, the hybrid polymers are considered environmentally safe and far superior to synthetic polymers if redesigned at molecular and nanoscale level to minimize the bioburden on aquatic life.

Keywords Fish-derived biopolymers · Biodegradable fishing gears · Functional foods · Biofilm packaging · Wastewater treatment

1 Introduction

Biopolymers are chemically derived from a wide array of animal, vegetal and microbial sources. These polymeric biomolecules include lipids, polysaccharides, polynucleotides, and polypeptides, consisting of monomeric units linked by covalent bonds to form larger molecules. The non-toxic biopolymer has been derived from diverse biological sources including plants, bacteria, seafood waste, chicken feathers and other organic matter from the fishing industry [1–4]. To be animal-specific, the fishing industry is the major contributor to the bio-burden of the aquatic environment, which can be reduced by using fish-derived biopolymer like chitin, chitosan, collagen, glycosaminoglycans, and hyaluronic acids [5]. The circular reinforcement of this fish-derived polymer is an alternative to polyethylene, because it generates low biodegradable waste, similar to plastic in functionality and appearance, and requires less energy consumption to manufacture packaging material. For instance, MarinaTex is a novel, odorless, translucent, and flexible biopolymer with good shelf-life is made from the fish waste, and red algae [6]. Similarly, the seafood waste with crustacean shells is used to prepare recyclable bio-sheets [7].

Fish is considered to be one of the nutritious diets in human food because it is an excellent source of high-quality protein, omega-3-fatty acids, various minerals like phosphorous, magnesium, selenium, iodine etc. [8]. The fish-derived biopolymers are used in the activities of petroleum drilling, deep sea exploration photography, seafood packaging, and other ecological products that can restore the osmotic adaptation in aquatic life and aids in microbial genera to adapt to the harsh environment. The most extensively studied fish-derived biopolymer is chitin and its deacylated derivative chitosan. Chitin is considered the most abundant polysaccharide available in nature. Another biopolymer is collagen, which is extracted from the scales and bones of fishes [9]. It has good tensile strength and majorly applicable in pharmaceutical, biomedical, and food applications. Moreover, when dried solid fish waste is biologically processed with the bacterium, *Bacillus subtilis* (KP172548), 1.62

gL^{-1} PHB (poly 3-hydroxybutyric acid) was produced [10]. Likewise, fermentation experiment of shrimp waste with the bacterium, *Salinivibrio* sp. M318 yielded 42% (w/w) PHB when fish oil was used as C-source and when the fish matrix was used as N-source, then the yield of PHB is 51.7% (w/w) [11].

1.1 Sources of Fish-Derived Biopolymers

The fish-derived biopolymers exist in several shapes, highly branched with low molecular weight and arranged intrinsically by delicate polysaccharides and proteins as a structural constituent of the skeletal system. Because of their complex polymeric structure bounded by glycosidic linkages, these polymers provide mechanical strength to the tissues and keep them intact [12]. The raw biopolymers belong to plant origin, microbial origin, agricultural wastes, fossil wastes etc. Also, they can be synthesized chemically from the monomer units such as amino acids, fatty acids, lipids, chitin, chitosan, proteins, DNA, RNA etc., that can be scaled readily at low cost, to commercialize processing of the biopolymers [13, 14]. Few of the biopolymers synthesized from microbes include chitosan (polyamides), polylactic acid (PLA), poly 3-hydroxybutyric acid (PHB), polyesters, polyphosphates, hyaluronic acid (HA) connected through linear polysaccharide chains bounded by hydrogen bonds [15]. They provide flexibility, tensile strength, and viscosity to the cells and act as a protective matrix.

The major biopolymer present/produced from fishes and its wastes include collagen (protein-based) such as hyaluronic acid (HA) and glycosaminoglycan (GAG), chitin, and its derivative chitosan (polysaccharide-based), and gelatin s found in various connective tissues of the body like scales, skin, bones, ligaments, tendons and cartilage [16–18] (Fig. 1). The collagen is responsible for drug and gene carriers. It is used as burn cover dressings as well in the wound healing process. Many researchers have diverted their studies to the extraction and characterization of collagens obtained from the various fishes like rabbitfish (*Chimaera monstrosa*), cuckoo ray (*Leucoraja naevus*), small spotted catshark (*Scyliorhinus canicula*), Atlantic grenadier (*Nezumia aequalis*), lantern shark (*Etmopterus* sp.), *Catla*, *Cirrhinus mrigala*. The collagen is extracted from the skin, bones, and fins of fish, which gets denatured at a low temperature (25–30 °C) as compared to mammalian collagen, which has a denaturation temperature difference of 9 °C i.e., (39–40 °C). The skin of the fish usually consists of type I collagen and is around 70% degree of purity depending upon the type of species, found in the various seasons and the fish has a capacity to retain the moisture and exhibits no irritation. Thus, fish collagen is an excellent source and can be used in dermal applications [19].

Chemically, chitin and chitosan are crystalline in nature and insoluble in common solvents, except the acidic solvent. They have strong inter/intra-molecular units of 2-acetamido-2-deoxy- β -D-glucose bounded by β (1–4) linkages. They are non-allergic in nature, therefore, suitable for controlled drug delivery systems, where they can

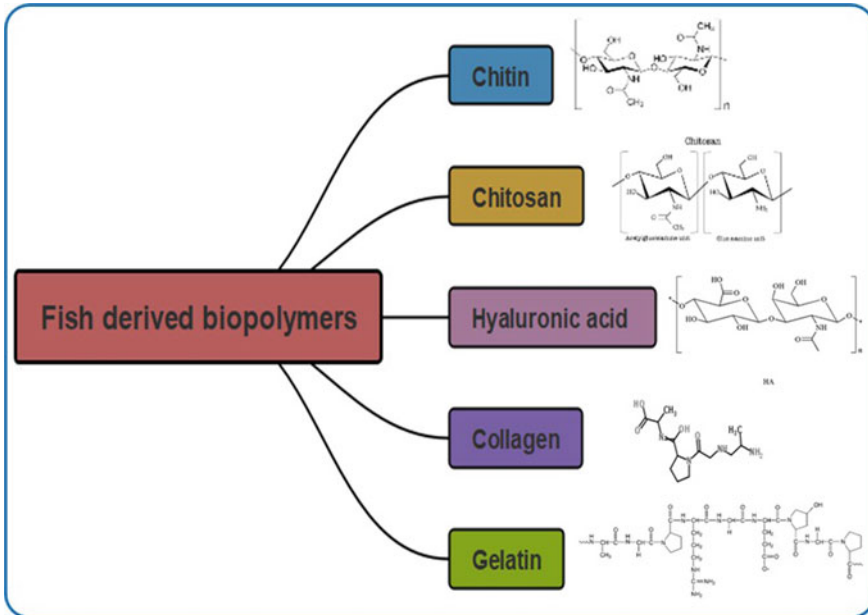


Fig. 1 Different types of Fish-derived biopolymers used in fishing industries

be used as protein-carrier (amino acids) and enzyme-carriers, and various types of packaging material [20].

1.2 Market Potential of Biopolymers in the Circular Economy

The fishing industry mainly depends on plastics for various activities such as fish luring, fishing nets, ropes, baskets, gloves etc. that further adds the cost of transportation from rural to urban areas. To reduce the financial burden, the proficient set-up of bioplastic plants near the fishing zone can lead to the sustainable development of the packaging industry and restore the environment.

The natural biopolymers obtained from marine sources have a minimum impact on food chain due to its high biocompatibility and rapid disintegration. Moreover, the natural biopolymers help in reducing the land and water pollution.

Also, in terms of employment, the biopolymers are advantageous to get profoundly skilled labour, and create ease of license for commercial fishing assignment with a monetary benefit. According to the global market report by Markets and Markets [21] it is estimated that the biopolymer market will grow to US \$27.9 billion by 2025 at the CAGR of 21.7%. The global growth highlights the potential of bioplastic in accordance with environmental concerns. This is a great opportunity to minimize dependence on conventional plastic and enhance the production of biopolymer [22].

The fish-derived biopolymer can provide a restorative solution to marine life, and meet daily human needs of toiletries, paper bags, food packaging material, bottles, textiles and many more [23].

The fish-derived biopolymers are used to make compostable barrier coatings, using equal combination of cellulose pulp from plant sources. This type of sustainable coating can be used in multiple packaging of food and feed in daily lives. The fish residue valorization towards zero-waste sustainable industry can replace the global plastic dependence in the future if it is unanimously implemented under the climate action program [24]. The notable leading market players in utilizing fishery waste and manufacturing bioplastic are NatureWorks, Italy; Braskem, Brazil; BASF, Germany; Biome plastic, UK; Toray Industries, Japan; Plantic Technologies, Australia; Tianan Biologic Materials, China and many more [25]. The successful use of biopolymer in everyday life might bring monetary ramifications but from an ecological point of view, it can balance nature degradation [26]. However, there are certain drawbacks of biopolymers that need to be addressed for universal acceptance, such as, low thermal and tensile strength, high moisture-holding capacity, compatibility, slow production process as compared to synthetic counterparts. To alleviate these disadvantages, a blend of polymers is done to increase their applicability at a larger scale and change the design of the biopolymer for its feasibility in biological degradability.

2 Types of Biopolymer in Fishing Industries

The recent advancement in the biodegradable films in the fishing industry based on their mechanical, barrier and antioxidant properties has gained popularity amongst many industrialists [27]. The significant attributes of biopolymers are stability, durability, feasibility and resiliency is further improved by incorporating graphene oxide, protein isolates, fatty acids, essential oils, and other cross-linkers. Natural biopolymers like starch, protein, cellulose, chitin, pectin, chitosan, lignin and collagen is obtained from animal and plant kingdom. Carbohydrate-based biopolymers are low toxic, renewable, biodegradable, and stable in nature; hence, frequently used commercially in pharmaceutical industries, cosmetic industries, fishing industries and so forth [22, 28]. The origin, physical appearance and role of biopolymer are listed in Table 1.

2.1 Chitin

Chitin is crystalline in nature; it is a microfibrillar polymer of glucose and extracted from the exoskeleton of insects, invertebrates, some fish cells, and wall of fungi. It is stable in alkaline solution and dissolves in acidic solutions only. A significant natural source of chitin is shrimp and crab, which are abundant in the seafood processing industry. The chitin biopolymer is mainly used in biomedical engineering to prepare

Table 1 Sources and applications of significant biopolymers

Name of polymer	Source of origin	Physical appearance	Role of biopolymers	References
Chitin	Crab, Shrimp and prawn	Translucent, pliable, resilient, and quite tough	Used in fishing and cosmetic industry	[29]
Chitosan	Shellfish and crustacean waste materials	Pale, white and flaky and its moisture content was 10.9%	Bioremediation of toxic phenolic product, promote osteogenesis, fat absorbent action, flocculating agent, purify drinking water, manufacturing, personal hygiene products, anti-bacterial, anti-acid, fat absorbent action	[30, 31]
Collagen	Exoskeleton of marine invertebrates	Hard, fibrous, insoluble, protein, and molecules form long, thin fibrils	Biodegradable matrices, solid support micro-carrier in the production of enzymes, Sutures, dental composites, sausage casings, skin regeneration templates, cosmetics	[32]
Gelatin	Fish, bones, pig skin	Translucent, water soluble, flavourless, moist and brittle when dry	Pharmaceutical and medical use, thickener, stabilizer, food wetting agent, emulsifier	[32]
Hyaluronic acid (HA)	Eyeballs of fishes (Tuna, Shark and Swordfish)	Transparent, viscous fluid or white powder, water soluble	Cosmeceuticals, anti-aging products, nutraceuticals, food ingredient, nanotechnological processes	[28–30, 33–35]

biomaterial that can repair and restore damaged tissue. Globally, the annual production rate of chitin from crustaceans and fish scale waste is estimated to be 10 billion tons. In coastal areas, the material form of chitin is a major source of beach pollution which is hard, inelastic and nitrogenous polysaccharides [36].

2.2 Chitosan

Chitosan is differing from chitin only by the acetyl content of the polymer. It is a modified natural biopolymer that is hard, non-toxic and cellulose-like fibre. A significant production material of chitosan is shrimp waste and other sources of chitosan are crustaceans, insects, fungi and some algae. Their excellent properties include biocompatibility, bioactivity, biodegradability, penetrability, anti-microbial activity, chelation, drug carrier for controlled release, film, and absorptive limit. It promotes bone tissue building, fat absorbent action decalcification of dental enamel, healing of ulcers and injuries and osteogenesis. It inhibits bacterial plaque formation [37]. Commercially, chitosan offers a wide range of applications such as in cosmetic preparation, biomedical, paper industry, food industry, textile industry, pharmaceutical, biotechnology, and biochemistry. It is also used to prevent food spoilage from microbe contamination, preparation of biofilms for food packaging, purify the water, and delay blanching of fruit juices [38]. Commercially, chitosan offers a wide range of applications in diverse industries including biomedical, cosmetic, paper, food, textile and biotechnological industry.

2.3 Collagen

Mammalian cells are rich in collagen protein, which is usually synthesized by fibroblast that originates from pluripotential adventitial cells or reticulum. A collagen molecule is a triple helical structure with a length of 300 nm and a width of 1.5 nm, respectively. The molecular weight of collagen, based on amino acid sequence is 300000 Daltons [39]. Collagen is rod-shaped molecule and accounting for about 20–30% of total body proteins and primary structural materials [40]. The collagen matrix is used in the treatment of severe burns and collagen sponges used in dressing for acute injuries, nucleic acid and protein transporters to assist bone repairs. In addition, collagen hydrogel is used as genetic material delivery carriers in biomedical applications. For example, thermostable collagen nanoparticles utilized as an anti-cancerous agent such as camptothecin and hydrocortisone bearer for parenteral administration and other therapeutic compounds [27]. Collagen has wide range of applications because of their diverse physicochemical properties such as high biocompatibility, low anti-genecity, non-toxicity and high biodegradability [41].

2.4 Gelatin

Gelatin is water-soluble, a sterile biopolymer that does not contain preservative and has a three-year expiration date at room temperature. Structurally, it is a heterogeneous polypeptide, forming a complex mixture of α -chains, β -chains and γ -chains. Gelatin is a synthetic colloid produced from the degradation of bovine collagen by incomplete hydrolysis of collagen removed from fish, pig skin and cow bones so forth. It is an important biopolymer that is colourless, translucent, flavourless food ingredients. It is extensively used in preservation of meat and fish-based products due to its good foaming, emulsifying and wetting properties [42]. Therefore, gelatin is widely used in food packaging industries owing to its exclusive functional and technical characteristics.

2.5 Hyaluronic Acid (HA)

HA is a water-soluble, translucent, high molecular weight biopolymer, which is only present in the eyeball and cartilage intracellular matrix of fishes. It is the only glycosaminoglycan member that is non-sulphated by alternating disaccharide units of N-acetyl-D-glucosamine and D-glucuronic linked by β -(1 \rightarrow 3) and β -(1 \rightarrow 4) glycosidic bonds [43, 44]. HA is highly used in the biomedical field due to its high biocompatibility in visco-surgery, controlled tissue permeation and hydration in arthritis treatment, and macromolecular carrier in cancer therapy, plastic surgeries and targeted drug-deliveries of intra-ocular surgeries. It has characteristic inflammation property that allows it to hold water molecules in limited space and provides lubricity to the tissues. Therefore, Hyaluronic acid has tremendous potential in regenerative medicine and cosmetology [45].

3 Commercial Applications in Fisheries

The fish gear should be reused for the sustainable use of biopolymers in the fishery industry (Fig. 2). The alternative approach to design fish binders, gill nets, fishing lines, traps etc. which should be transparent, flexible, dissolve in water after few days and possess superior permeability to prevent ghost fishing. The biopolymer fishing gears can halt the vicious circle of death of fishes and other aquatic animals by derelict nets, and boost ecological restoration of waterbodies and aquatic life [46].

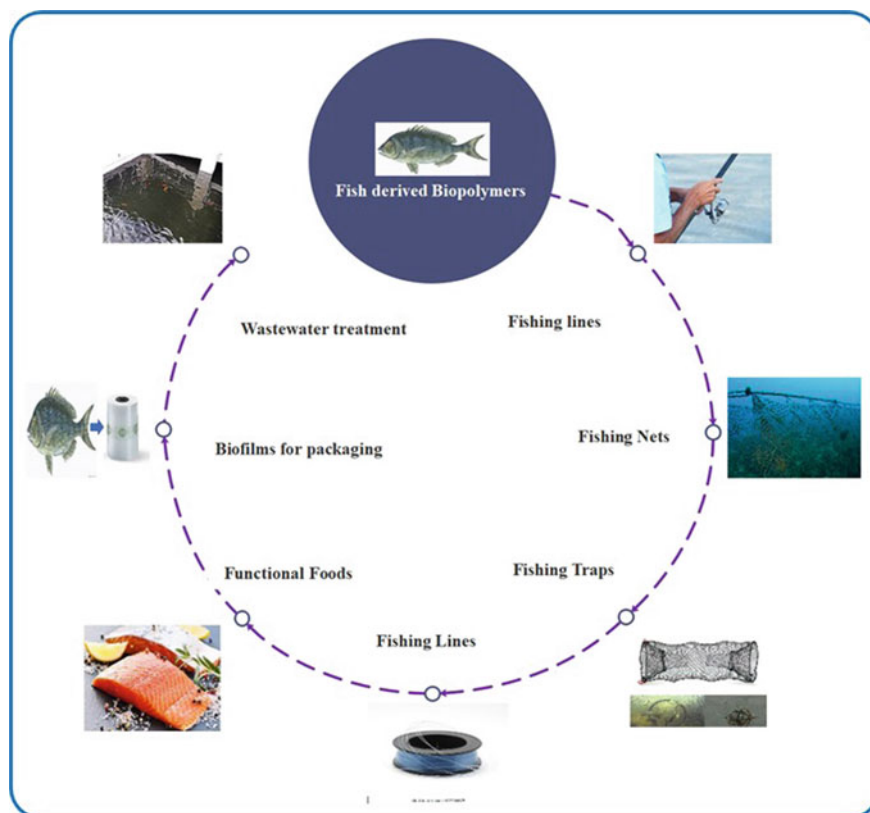


Fig. 2 Applications of fish-derived biopolymers in fisheries

3.1 Fishing Lines

Most of the fishing lines or ropes are made from synthetic polymers as they are single-stranded, strong, thin, and available in different colors to distinguish from other fishing lines. The synthetic polymer causes more harm to the fishes as they do not degrade and form a lump of fine network at the fishing place, further entangling and injuring the fishes and rest aquatic life. To overcome this situation, the biodegradable fishing lines were designed with natural materials such as polyglycolic acid resin (PGA) filament with high tensile and knot strength. These PGA filaments when mixed with *PLA*, *p*-dioxanone, and ϵ -caprolactone make it more heat resistant and firm. The monofilament of PGA also gave good results with blends of polybutylene succinate (PBS) and polybutylene adipate-co-terephthalate (PES) to yield optimal strength under seawater [47]. These fishing lines if left in the water bodies for more than a fortnight, they will maintain 25% of the original tenacity [48]. The successful brands of eco-friendly fishing lines, in the form of filament, fluorocarbon and braid (hybrid)

are Toray, Eagle claw, Fieldmate showed a remarkable four-month biodegradation time.

3.2 Fishing Nets

Globally, the nylon nets are widely used as a fish gear. Despite its wide use, it is abandoned in the sea for a longer duration as it needs physical labor. According to the technical report available online, on average 13,941 gillnets are lost each year. Because of this, there are a negative effect on the benthic environment, navigational problems, marine litter, and plastic pollution.

To reduce this problem, the Norwegian Directorate of Fisheries has initiated a gear disposal and recycling program named Abandoned, Lost or Discarded Fishing Gears (ALDFG) and retrieved 20,450 lost gillnets and other fish gears [49]. Traditionally, the biodegradable fish nets were designed using a blend of 82% polybutylene succinate (PBS) and 18% polybutylene adipate-co-terephthalate (PBAT), which were tested for their catching efficiency for a longer time duration of 6–42 months [46]. As compared to conventional gear made of Nylon polyamide, polyester, polyethylene, and polypropylene; the biodegradable fishing nets started biodegradation into natural materials by the action of microorganisms and lose their ghost fishing capacity after few months of underwater exposure. However, the fishing performance and stiffness of biodegradable nets is lower with respect to nylon nets. Therefore, projects like Innovative Fishing Gear for Oceans (INDIGO), funded by the European Union is undergoing to design 100% biodegradable fishing net with a controlled lifespan [50].

3.3 Fishing Gear and Traps

As per the FAO [51] technical report, it is estimated to discard approximately 6.40,000 tonnes of all fishing gear in the oceans annually in bad weather conditions. The fishing traps are made to catch fish during low tides. It is usually made of steel boundary vessels, with sufficient enclosed space to house targeted fishes for their smooth entry and barricaded exit. Polyhydroxyalkanoate (PHA) is also used as trap apparatus and degrades naturally if continuously submerged for many months [52]. Currently, the biodegradable fishing trap derived from cellulosic derivatives such as polysaccharides, chitin or chitosan are widely used in fishing industry as it readily dissolves in the water in few days and prevent unwanted fish mortality [52].

3.4 Fishing Lure

The artificial fishing lures are well fabricated by fine plastics of PVC or silicone rubber. Such lures do not get digested in the fish body and thus become aquatic pollutants. They also affect the growth and development of fish by hindering its gastrointestinal tract and can eventually led to the death of the fish. The biodegradable, semitransparent, and the soft lure is made by molding like worms using jelly chitosan, water-soluble gum, cereals starch, soy protein, etc. Further, the addition of marine fats and oils, to the bait attracts the fish and makes the process less time-consuming. The PVOH polymers as hydrogel matrix of soluble capsules, which are prepared by mixing carrageenan and gum, is biodegradable, transparent, and used mostly in recreational fishing activities [53]. The biological lures can control the bait release in an effective way, as an aquatic feed in farmed fisheries.

4 Industrial Applications of Biopolymers

The fish-derived biopolymers can be valorised to produce various useful materials.

4.1 Functional Foods

Several edible marine invertebrates, including cuttlefish and sea cucumber, are promising potential ingredients as functional foods [54]. Many researchers have reported that chitin and chitosan (biopolymer) derived from these edible marine invertebrates exert a broad spectrum of bioactivities, namely antioxidant, antimicrobial, anticoagulatory, anticancer, hypocholesterolemic and wound healing properties [55, 56]. These bioactivities of chitin and its derivative have been mainly attributed to its physical and chemical properties, including molecular weight, functional groups and deacetylation degree [57].

Chitin is used as a health supplement in the form of capsules due to its exceptional lipid metabolism capacity [58]. Kuprina et al. [59] have developed a functional food from a mixture of pollock and salmon belly minced fish meat with the biologically active chitin mineral food supplement “Hizitel”. Azuma and Ifuku [60] suggested that chitin nanofibers (CNFs) and surface-deacetylated chitin nanofibers (SDACNFs) are promising functional food for patients with inflammatory bowel disease or obesity. The authors observed that CNFs substantially ameliorate the clinical symptoms of IBD. SDACNFs reduced the levels of leptin in serum and repressed the rise in body weight.

Chitosan increases the nutritional benefits of the food products, including boosting immune response and glucose-lowering effect while maintaining the organoleptic properties of the product [61–63]. Chitosan is a promising source of dietary fibre in

organisms that lacks a specific chitinase enzyme in their gastrointestinal tract [64]. Lie et al. [65] reported that the feed supplementation with high molecular weight chitosan decreased fatty deposit in liver, spleen, and muscle of broiler chickens. Qinna et al. [66] suggested a new functional food containing chitosan (1%) and pectin (5%) as an alternative to meat. Anandan et al. [67] found that dietary supplementation with chitosan had a protective effect on lipid oxidation in induced myocardial infarction in rats.

Microcrystalline cellulose (MCC) biopolymer is broadly considered as a functional ingredient in several food products, including dairy, bakery, and confectionary [68]. The colloidal MCC contains 98 g/100 g of insoluble dietary fibre [69]. The experimental animals fed with MCC fortified diet showed a reduced level of cholesterol [70]. MCC fortified food also plays a substantial role in the management of obesity and diabetes mellitus via hypolipidemic and hypoglycemic effect, respectively [71]. Cellulosic nanomaterials (CNMs) biopolymer is extensively utilized in nutraceutical and food industry because to its exceptional physico-chemical properties, namely high mechanical strength, lightweight, and biocompatibility [72]. Bacterial cellulose (BC) biopolymer is widely used as a resource of dietary fibre, and it is approved as a “generally recognized as safe” food by the U.S.FDA [73].

4.2 *Biodegradable Preservative and Packaging*

Seafood is a rich source of functional health-promoting compounds, including vitamins (vitamins D, B and A) and polyunsaturated fatty acid [74]. However, seafood products are highly perishable, and it is most prone to degradation by microbiological, enzymatic, and chemical reactions. Currently, chitin and chitosan biopolymer are used as an alternate biodegradable natural preservative for retaining seafood quality and increasing the shelf-life of seafood-based products [74]. Generally, chitin and chitosan increase the shelf life of marine-based products by improving oxidative stability, reducing lipid oxidation, and inhibiting the growth of microorganisms.

Chitin biopolymer is used as an edible coating in food safety as it principally maintains the sensory characteristics of food material. Moreover, chitin is also used as a support matrix for enzyme immobilization that imparts remarkable operational stability in the food processing industry [74]. Morganti [75] has developed chitin-based biodegradable food packaging material by using chitin nanofibrils. The combination of polylactic acid and nanocellulose biopolymer is also used as a novel promising sustainable eco-friendly food packaging material [76].

Chitosan is widely used as a packaging material component, additive and coating agent for seafood-based products because of its distinctive functional and physico-chemical properties [77, 78]. Several researchers have demonstrated that chitosan-based coatings help in maintaining the physico-chemical properties of fish and other seafood-based products [78]. Sathivel et al. [79] documented that an edible coating of 1 or 2% chitosan biopolymer suspended the degree of lipid oxidation in *Oncorhynchus gorboscha* during frozen storage. Kumar et al. [80] demonstrated that

the chitosan can be used as an encapsulation biomaterial for several sensitive products, including fish oil due to its noticeable emulsification capacity. Benjakul et al. [81] concluded that chitosan can enhance the gelling properties of marine-based products, including fish surimi products. Kok et al. [82] observed that chitosan (1%) constrained the growth of microorganisms in fish ball throughout 21 days of storage. Ye et al. [83] showed that chitosan-coated plastic films inhibited the growth of *Listeria monocytogenes* on salmon for at least 6 weeks. Mohan et al. [84] revealed that the edible chitosan coating (1 and 2%) improved the textural properties, water holding capacity, drip loss, and inhibited the bacterial growth in *Sardinella longiceps* during cold storage conditions.

Numerous researchers have repeated that chitosan-based coatings could impede the production of trimethylamine—nitrogen in marine food by inhibiting the growth of microorganisms [85, 86]. Chitosan has been used as an edible coating or film in marine-based products owing to its tremendous film-forming ability. Moreover, it is used as an antimicrobial and antioxidant agent in seafood-based products [87]. Chitosan-based coating is used as a preservative in seafood products due to its remarkable ability to reduce the increase in pH value [88]. Several studies have reported that chitosan-based coatings can increase the quality, sensory attributes (taste, odour, colour, appearance, texture, flavour and elasticity) and shelf life of seafood products [88]. Therefore, chitosan-based biopolymer possesses promising prospects in food preservatives and food packaging industries.

4.3 Wastewater Treatment

Wastewater contains heavy metals, dissolved and particulate matter, solids, micropollutants, nutrients, and microorganisms in a complex matrix [89]. The water is generally contaminated through various industrial processes, agricultural and domestic activities (swimming, boating, and fishing etc.) [90–92]. The contaminated wastewater is highly toxic and can adversely affect the organisms [93–95]. Therefore, it is of paramount importance to develop effective strategies for treating wastewater [96–98]. Additionally, in the current scenario, wastewater treatment is highly critical due to dwindling water supplies, tougher discharge regulations, and rising wastewater disposal costs [99]. The primary aim of wastewater treatment is to remove as many dissolved solids as possible before discharging the residual water (effluent) into the environment. Conventional wastewater treatment encompasses pre-, primary-, and secondary-treatment [100]. However, the conventional methods lack accuracy, cost-effective discharge standards and desired level of purification [101]. Over the last few decades, natural biopolymers including chitosan, chitin and cellulose have garnered tremendous interest in wastewater treatments due to their high efficiency, low-cost, high mechanical stability, abundance, renewability, biodegradability, and high porosity [102, 103]. The different biopolymers used for wastewater treatment are summarized in Table 2.

Table 2 List of different biopolymers used for the treatment of wastewater

S. no.	Biopolymer-based material	Wastewater treatment	References
1	MWCNTs/SnO ₂ decorated cellulose nanofiber	Removal of Cu (II) from wastewater	[115]
2	Natural cellulose fiber	Sorbent for lead in wastewater	[116]
3	Reactive polyhedral oligomeric silsesquioxane nano-cellulose hybrids	Adsorption removal of Cu ²⁺ and Ni ²⁺ from wastewater	[117]
4	Cellulose-Based Solid Acid	Absorption of heavy metal ions from printing wastewater	[118]
5	Cellulose-based membrane	Adsorption of liquid waste dyes and chromium	[119]
6	Chitin/polyethylenimine biosorbent (CH-PEI)	Removal of uranyl-carbonate compounds from water	[120]
7	Chitin-glucan nanopaper	Adsorption of heavy metal ions	[121]
8	Chitin/chitosan nano-hydroxyapatite composite	Removal of copper (II)	[121]
9	Chitosan microspheres	Selective heavy metal removal	[122]
10	Chitosan bed columns	Removal of arsenic	[123]
11	Chitosan and duckweed combination	Removal of boron	[124]
12	Chitosan-clay nanocomposites	Removal of Cu (II) from aqueous solution	[125]
13	Magnetic nanoparticles of chitosan modified with polyhexamethylene biguanide	Removal of hexavalent chromium from aqueous solution	[126]
14	Novel chitosan based thin sheet nanofiltration membrane	Rejection of heavy metal chromium	[127]

Chitosan biopolymer has widely used an adsorbent for removing several pollutants from wastewater, including heavy metals and dyes, because of its high degree of deacetylation that promotes higher interaction of free amine groups with the pollutants. It is also considered to be an efficient bio-sorbent towards several other contaminants because of its hydroxyl group enriched structure [104]. Chitosan is also an ideal alternative substitute to conventional synthetic materials for the treatment of effluents in agricultural wastewater, such as residual pesticides, herbicides, and fertilizers. Pambi and Musonge [105] suggested that chitosan is a suitable low-cost biodegradable material for treating wastewater from sugar industry by performing a dual role of coagulant and flocculant through its relatively high molecular weight and charge density. Crini et al. [106] reported a novel direct bioflocculation method for treating wastewater from paper and pulp industry by using low-cost chitosan. Ahmad et al. [107] effectively remove the solids from palm oil effluent using flake and powdered chitosan. Altaher [108] successfully remove the turbidity from seawater by dissolving chitosan in hydrochloric acid. Dima et al. [109] reported that reticulate

chitosan micro/nanoparticles can efficiently remove the toxic Cr (VI) from seafood processing waste.

Gopi et al. [110] have successfully developed cellulose nanofibers (CNFs) based bio-aerogels for specific adsorption of methylene blue and rhodamine 6G from wastewater. Albukhari et al. [111] purified nitrophenol and dye-contaminated water using silver nanoparticles@cellulose acetate paper prepared by impregnation method. Zhou et al. [112] used magnetic cellulose powder for purifying dye-polluted water-ethanol combination. Garcia et al. [113] immobilized laccase on chitosan and alginate-based matrix for effective removal of 17α -ethinylestradiol from water. Chitosan-silica nanoparticles have been successfully developed for catalytic degradation of 1,1-dimethylhydrazine from wastewater [114]. Overall, natural biopolymers have demonstrated prodigious potential in wastewater treatment.

5 Conclusion and Future Perspective

The multiple applications of fish-derived biopolymers have widened the scope of the circular economy of the fishing industry. Over the last few years, the nanotechnological advancement of biopolymers has been exploited to purify wastewaters. This treatment is environment friendly as it avoids chemical substances, thus safe for flora and fauna of the aquatic system. The treated wastewater is free from toxic micropollutants, dyes and pesticides and reusable for seafood processing. More specifically, seafood is highly perishable, and the biofilm packaging enhance the shelf-life of the food product without compromising the organoleptic characteristics. The edible coating is thermostable, pH stable, resistant to bacterial growth and a good emulsifier to be considered for food processing and packaging material.

Another promising industrial application is to prepare functional foods by blending fish waste with biopolymers. This can be used as a dietary supplement as it is rich in protein, omega-3-fatty acids, dietary fibres and minerals and GRAS in bakery, confectionary, and nutraceuticals. Because of the biocompatibility, elasticity, translucent and odourless characteristics of chitin, chitosan, collagen, gelatin, and hyaluronic acid are potential candidates for biomaterial. This soluble biopolymer is suitable for fishing gears as it will reduce ghost fishing incidents and reduce the physical activity of collecting submerged fishing nets/lines. The latest technologies involve hybrid polymers that need less time and energy to produce with superior flexibility and strength to lessen the dependence on plastics. As mostly fishing gears and plastic-based and many companies are working together on more sustainable ways to produce completely biodegradable products. However, many challenges like increasing the catching capacity of fishes, using biopolymeric fishing nets; low tensile strength of fishing lines; high water holding capacity of fishing lures which leads to microbial degradation etc. are needed to be addressed.

Therefore, the future study needs in-depth analysis on the structural and functional aspects of biopolymer to be reinforced in the fishing industry as an alternative to polyethylene. Despite all the challenges, the biopolymer prototypes need to be exclusively developed for efficient drug-delivery systems in medical and pharmacological products. In addition, the promotion of biopolymers in the fishing industry community will further reduce the global bioburden.

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Biopolymers in Cosmetics, Pharmaceutical, and Biomedical Applications



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Abstract Biopolymers have been extensively explored as a potential class of material for wide range of applications owing to its excellent biomimicking characteristics. The biopolymers are found in natural environments with ideal physicochemical properties such as stretchability, plasticizing ability, pseudoelasticity, and unique bioactive properties like biocompatibility, biodegradability, non-carcinogenicity, non-immunogenicity, and antimicrobial nature that makes them ideal biomaterials. However, these properties greatly vary based on the source, method of isolation, structure, molecular weight, etc., that significantly influence the activity of the biopolymer. Various advanced technologies are being adopted for extracting and processing biopolymers for enhancing their activity and developing them into smart materials for immediate biomedical applications. The bioactive properties aid their applicability as scaffolds, implants, sustained drug release carriers, bioimaging, while for cosmetic applications owe to their biocompatibility and enhanced bioactivity as they can be readily modified as moisturizers, creams, serums, and dermal patches. This chapter discusses the different properties of biopolymers from animal, plant, and microbial origin to develop them as novel molecules for cosmetics, pharmaceutical, and biomedical applications.

Keywords Biopolymers and their origin · Physicochemical properties · Bioactivities · Potential applications

1 Introduction

Polymers of both natural and synthetic origin have gained huge attention in the past few decades making it a popular choice in various biomedical, cosmetic, industrial, and pharmaceutical applications. Polymers obtained from natural sources are termed

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as biopolymers and are composed of covalently bound repeating monomeric units. They are broadly classified based on their origin of isolation (see Fig. 1). Polymers such as chitosan, collagen, gelatin, hyaluronic acid, etc., are mainly extracted from animal sources and are known to possess higher biomimicking properties like similarity with extracellular matrix components, higher cell adhesion properties and biocompatibility. Plant-derived biopolymers such as starch, alginate, and fucoidan exhibit higher antioxidant and antimicrobial properties with minimum immunogenicity. While biopolymers derived from microbial systems like exopolysaccharides, alginate, and cellulose show biodegradability, tunability, reactive surfaces, viscoelasticity, plasticizing ability, and porosity.

Structurally, the biopolymer backbone is composed of carbon, oxygen, and nitrogen atoms making them easily biodegradable. They are preferred compared to synthetic polymers due to its compatibility and abundance in different biological systems, effective replacement for synthetic materials with minimal environmental damage and cost-effectiveness. The chemical structures and organization of biopolymers are very alike to the macromolecules native to the extracellular environment. Thus, making them biocompatible with various biological systems showing minimum or no toxicity, immunogenic, or carcinogenic responses in addition to desirable biofunctionality compared to synthetic polymers [1] (see Fig. 2).

Extensive research is involved in developing these materials as they can be easily modified, produced economically to meet various biomedical and industrial demands. For instance, these biopolymers are easily tuneable for industrial applications due to their gelation ability on addition of metal ions like Ca^{2+} , Cu^{2+} , Zn^{2+} , and Mn^{2+} [2]. The presence of functional moieties like hydroxyl, amino, and carboxyl in natural polysaccharides make them ideal materials for stimuli responsiveness and varied chemical conjugations [3]. By virtue of their physical and chemical properties biopolymers have been an ideal candidate for application in tissue engineering. Their nontoxic, biodegradable, biocompatible, and non-immunogenic nature along with their ability to maintain moist environment, absorption of exudates and hemostatic

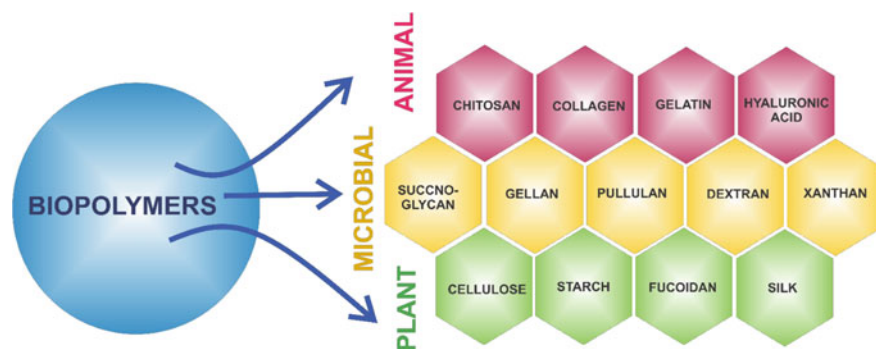


Fig. 1 Classification of biopolymers based on the source

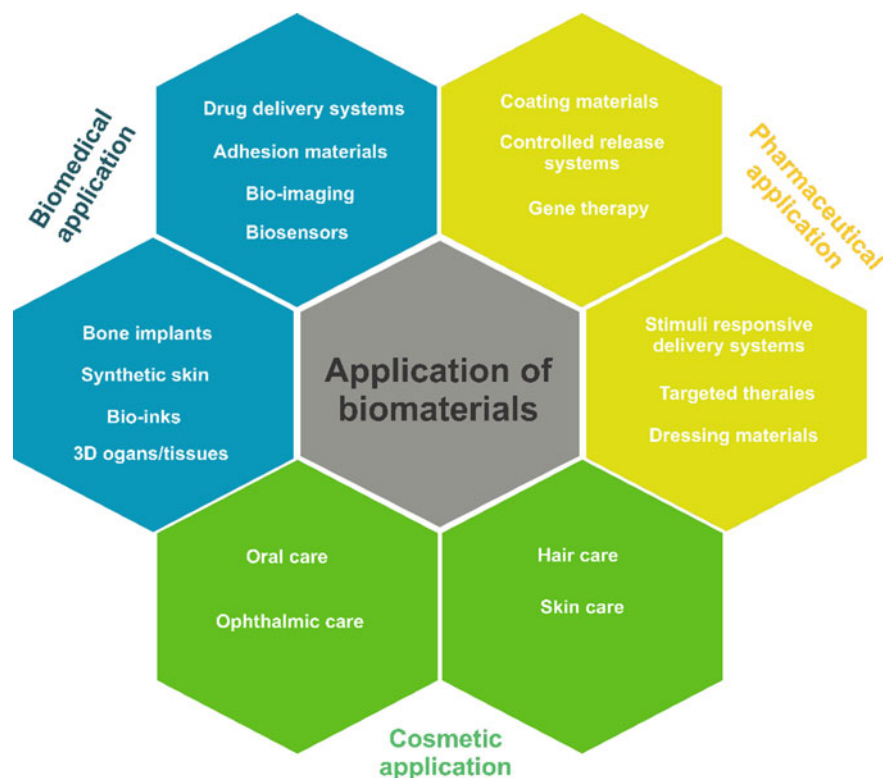


Fig. 2 Application of biomaterials: Biomedical, Pharmaceutical, and cosmetic application

nature enable their use as scaffolds for wound healing applications [4]. The fourth-generation scaffolds are represented by the biomimetic materials that possess unique characteristics like immunological inertness, ability to replace the native tissue, and enable signal exchange in the host environment [5]. For biological applications principally, the biopolymers are combined with bioactive molecules like protein, lipids, cell types, or commercial drug to form scaffolds, hydrogels, nanofibers, nanoparticles for achieving targeted delivery, sustained drug release, and higher compatibility with the biological system. Natural polymers due to their thickening, gel forming, and stabilizing ability play an important role in controlled release of drugs. Recombinant DNA technology has enabled the development of protein drugs and here the natural polymers are of interest. As majority of the biopolymers possess extracellular matrix mimicking properties enhancing cell adhesion and proliferation, many biopolymers-based systems are being developed and its activities are assessed using cell and animal models. At times, two or more biopolymers will be used in combination for developing stable drug carrier systems, 3D systems imitating human cells or tissues and can also produce a synergistic effect.

Development of materials for protein drug delivery is possible by incorporation of biomaterials under conditions that minimize their denaturation and they also help in protecting proteins from physiological degrading agents until their release [6]. In recent times, materials are designed to function with response to external stimuli like pH, temperature, ionic composition and these polymers are called stimuli-responsive polymers making them suitable for various applications. These materials are extensively used as drug delivery systems, mediators for adhesion, matrix for encapsulation of bioactive materials, etc. The presences of biomolecules that inhibit the activities of hyaluronidase, matrix metalloproteinase, and elastase and collagen expression are applicable as skin anti-aging agents [7].

Production of majority of the biopolymers has been standardized at an industrial scale and is available commercially. Research evidences support their ability to readily modify into different systems that have been validated experimentally, yet only few of these biopolymers have been successfully utilized for developing into products of commercial interest for desired applications. In this chapter, we have disused the unique properties and potentials of different biopolymers that have attracted considerable technological interest, especially for cosmetics, pharmaceutical, and biomedical applications.

2 Biopolymers of Animal Origin

2.1 Chitosan

Chitosan and its derivatives have been well explored and is obtained by the deacetylation of chitin commonly isolated from crustaceans, exoskeleton of insects, cell walls of fungi and bacteria. It is composed of β -(1,4)-linked N-acetyl-glucosamine units [8]. Structurally, chitosan can chemically be modified at three active sites to obtain desired activities. These include two hydroxyl groups and an amino group whose chemical modification yields desired solubility, physical and mechanical properties for various applications. Hence, the site of modification is chosen as per the desired application to develop biodegradable, biocompatible, bioadhesive, and biorenewable materials. Chitosan is isolated by fermentation processes, enzymatic processes, while harsh thermodynamic process is employed for commercial production. The quality is determined by the chitin source, degrees of deacetylation, and method of separation. Commercially, it's available in different molecular weights, purity, and physicochemical properties [9]. It is positively charged, water-insoluble, possess high thermal tolerance with wide optimal pH range, nontoxicity to cells, and biodegradable properties make it suitable for various biomedical, pharmaceutical, and cosmetic applications. In recent years, huge attention has been given to chitosan-based nanoparticles, films, hydrogels, and 3D scaffolds formed readily by

modification of its structural backbone [10]. Dressing, hydrogels, and nanocomposite scaffolds containing chitosan nanoparticles showed higher hemostasis, anti-necrotic activity; wound healing and antibacterial activity. Several attempts were made to achieve enhanced wound healing with anti-inflammatory activity, antimicrobial activity, growth factor release, and peptide release, by incorporation of various bioactive materials on to chitosan-based carrier system for skin and bone tissue engineering. For cosmetic applications, its high molecular weight with cationic nature is proven to be ideal as it can prevent its penetration across the skin surface and interact with negatively charged skin. Additionally, its higher viscosity, solubility in acidic aqueous media, moisture-retention properties, film-forming, antimicrobial, and sustained release properties make it desirable for various cosmetic applications. For example, Afonso and colleagues prepared chitosan masks loaded with annatto (*Bixa Orellana* L.) and vitamin C with antioxidant and anti-aging properties [11, 12]; similarly, chitosan and chitin fibers for hair regeneration [13]. For pharmaceutical applications, chitosan-based patches have been fabricated for transdermal delivery of drugs; buccal patches for delivery of PVP K-30; stable polyaniline-Chitosan Patches for cardiac muscle conduction; chitosan-based toothpaste formulations with activity against *S. mutans*; chitosan-based foams with excellent rheological characteristics for preventing bleeding [14].

2.2 Collagen

Collagen is the most abundant macromolecule found in mammals like pigs, cattle, and humans present mostly in different connective tissues extensively contributing to the structural frame work. Its versatile properties and easy extraction from different marine organisms like seaweeds, sponges, and fish have made it a popular biopolymer of choice. They are briefly composed of three polypeptide chains, i.e., two α and β chain composed of glycine, proline, and hydroxyproline and has a molecular weight of approximately 300 kDa [15]. More than 29 types of collagen are commercially available and a few are distributed in various tissues identified and classified based on their structure. For tissues engineering and regenerative applications, use of different collagen types as matrix are thoroughly explored in various biological system as they can regulate various cell types and tissue functions. Collagen has been extensively used for various pharmaceutical and biomedical applications as they can be easily molded in to 3D structures by simple cross-linking or self-assemblies to form strong fibrous structures [16] along with excellent biocompatibility, bioavailability, and biodegradability. Type I collagen is predominant in skin tissues and collagen from marine origin are rich source of type I collagen. Different types of collagen delivery systems like patches, films, and scaffolds loaded with curcumin nanoparticles; growth factor delivery for skin and bone healing applications have been explored in laboratory studies. Owing to its natural moisturizing, regeneration, and film-forming properties collagen is a key component used in various cosmetic formulations. To prevent aging and restore collagen in skin, collagen-based sub-cutaneous fillers are

commonly used and are proven to be biodegradable, safe with reproducible effects [17]. Further, acidic pretreatment of collagen yields gelatin A and an alkaline pretreatment yields gelatin B with higher carboxylic acid content. They are biocompatible and biodegradable whose stability is improved via cross-linking [18].

2.3 *Hyaluronic Acid*

Hyaluronic acid (HA) is a non-sulfated glycosaminoglycan composed of repeating units of d-glucuronic acid and N-acetyl-d-glucosamine connected by alternated by β -1,4 and β -1,3 glycosidic linkages. HA is well distributed in mammalian tissue and cells and is also found in certain bacterial sp and is composed of 500–50,000 monosaccharide residues with molecular weight ranging between 10^4 and 10^7 Da [19]. HA is anionic due to the presence of carboxylate groups and readily binds to a large water molecules providing support to the extracellular matrix and forming a highly viscous gels. It is present extensively in the extracellular matrix of cells, synthesized by hyaluronan synthase (HAS), and degraded by hyaluronidases. The extraction processes and its physicochemical properties are extensively optimized and studied for various applications. HA is commonly isolated from umbilical cord of humans, bovine vitreous humors, various species of bacteria, green algae, molluscan, etc.; bulk HA production for industrial applications explore bacterial fermentation of various genetically modified strains [20]. HA obtained from animal tissues have high molecular weight whose degradation yields low molecular weight HA and its binding to CD44 cell surface receptors on the cell plasma membrane initiates diverse biological activities based on its molecular weight [21]. HA has high viscoelasticity, moisture retaining ability, biocompatibility, and its high molecular weight making it suitable for various applications. Due to their ideal properties and high safety profile, HA-based products are popular in the market, while few other potential products are being clinically tested for developing in to marketable products. HA can be readily modified via chemical modification like cross-linking to fabricate fibers, hydrogels, viscoelastic solutions, nanosuspensions, sponges, etc., for various preclinical and clinical applications to target wound healing, bone regeneration, drug delivery, and bioprinting. HA-based scaffolds hydrogels sponges and fibers loaded with osteoconductive protein BMP-2 and other growth factors like EFG, VEGF evaluated in vivo confirmed better bone and skin regeneration efficacy. HA has been extensively used in bioprinting technologies to construct different tissues or organs for tissue regeneration applications. HA is readily taken up via CD44, reported for regulating angiogenesis in tumors. Thus conjugation of HA with different anti-cancer drugs like doxorubicin and cisplatin. Biopolymer-based 3D printing has been extensively used to develop artificial tissue or organ to mimic intrinsic structures for tissue engineering and regenerative medicine. Lee J et al. developed HA-based hybrid bio-ink with rapid gelation compared to the conventional HA hydrogels requiring longer time. Cells like fibroblasts were viable up to 7 days in addition to enhanced angiogenic and osteogenic

activity in the mesenchymal stem cells cultured on the developed bio-ink [22]. Similarly, Hauptstein J and teammates developed HA-based bio-inks by UV cross-linking with improved and uniform extracellular matrix deposition in cartilage [23]. HA, due to its ideal viscoelasticity, high moisture restoration, and biocompatible properties, they are used for various ophthalmologic applications like preparation of eye drops for patients with dry eye disease; ocular drug delivery systems for delivery of dexamethasone for managing ocular inflammations; HA-based nano-carriers with higher mucoadhesiveness for delivery of dorzolamide hydrochloride and timololmaléate for treating glaucoma and HA-coated albumin nanoparticles loaded with Apatinib for enhanced topical delivery targeting diabetic retinopathy. HA, being predominant component of the ECM and owing to its non-allergenic and non-carcinogenic properties, is widely used as soft tissue filling agent. Currently, many HA-based dermal fillers are available in the market (Hylaform[®], Hylaform[®] Plus, Captique, etc.), while few others (Restylane[®] Perlane[®], Restylane[®] Fine Lines, etc.) are under clinical evaluation for its safety and efficacy [24]. Various laboratory and clinical studies have shown encouraging results exploring possible potential of developing HA-based derivatives for biomedical, pharmaceutical, and cosmetic applications.

2.4 Silk Proteins

Silk proteins are interesting biomaterials that are lightweight, very strong, and elastic with exceptional mechanical properties. Silk fibers are protein-based biopolymer filaments secreted by specialized abdominal glands via spinnerets, spigots, or ducts. Silk proteins are chiefly isolated from silkworms and spider dragline. Mass cultivation of silkworms by sericulture aids as rational economic source of silk biopolymer. India is the second largest silk producer in the global market, cultivating, and isolating silk from *Bombyx mori*. Silkworm proteins are mainly composed primarily of fibroin proteins and glycoprotein sericin adhering to fibroin. Sericin is amorphous in nature and is isolated by a thermochemical process called degumming. It serves as stabilizer in cosmetic and food industries, as mitotic influencer for cells, anti-cancerous drug, and anticoagulant as biocompatible undercoat. Fibroin, post-extraction is commonly used as silk protein with excellent shelf life with wide range of applications.

The spider silks are complex protein biopolymers with complex microstructures, both possessing great tensile strength and high elasticity [25]. The core fibers of dragline silks contain more than one protein, with high molecular weights produced by ampullate glands. Exceptional mechanical properties, biocompatibility, and well-regulated biodegradability facilitate the use of silk proteins in various biomedical, pharmaceutical, and cosmetic applications. Silk proteins in aqueous form are used for different applications. There are various isolation procedures and in order to get desired yield and activity the downstream processing for isolation is crucial. Silk biomaterials are widely used for skin or bone tissue modeling, electronic diagnostic devices, and implantable optical systems [25].

Several studies have examined the applicability of silk protein for biomedical and pharmaceutical applications owing to enhanced biocompatibility with negligible adverse effects in vivo. Aqueous fibroin solution can be used for developing injectable hydrogels, porous scaffolds, microsphere and implants ideal for tissue regeneration. Injectable nanohydrogels showed continued release of desferrioxamine suitable for tissue engineering applications. Electrospun silk fibroin fibers were fabricated for stabilizing human platelet lysate for sustained release showing enhanced fibroblast proliferation for wound care application. Microneedles of silk fibroin were prepared for vaccine delivery to immunocompetent tissue in skin against influenza, *Clostridium difficile*, and *Shigella*. The microneedle system from *Bombyxmori* holds ideal properties such as mechanical strength and biocompatibility. Their mechanical properties can mimic target tissues like skin and bone and can be easily degraded to form nontoxic by-products. The silk sericin protein-based serum substitute was developed as an additive in cell culture for cryopreservation owing to its good hydrophilicity and biological safety. Silk sericin are easily degraded by proteolytic enzymes, high moisture holding, ideal gelling properties along with high molecular weight making its suitable for various pharmaceutical and cosmetic applications. It readily forms emulsions and are used as stabilizers for pharmaceutical formulations. On undergoing sulfonation, they show anti-thrombotic activity times along with wound healing activity and can be easily developed into wound healing formulations. The mulberry silk of *Bombyxmori* is clinically used Uni-Graft W with improved clot strength [25]. The biocompatible, biodegradable, antibacterial, antioxidant activity, anticarcinogenic effects, UV protective properties, and moisturizing properties of sericin has attracted its use for cosmetic formulations for developing skin, nail, hair care, and ophthalmic formulations. Its resemblance with natural moisturizing factor has led to the development of silk sericin-based moisturizers. Sericin gels were prepared using sericin solution with pluronic and carbopol as stabilizers enhanced essential moisturization of skin by restoration of the amino acids. A V Daithankar and colleagues developed silk hydrolysate with water and sodium chloride moisturizer. It increased state of hydration in cells and showed no allergy with high biocompatible in skin and rabbit eye [26].

3 Biopolymers of Plant Origin

3.1 Alginate

Alginate is an anionic, hydrophilic linear polymer and is composed of (1–4)-linked β -D-mannuronic acid and α -L-glucuronic acid monomers. The polymer chain is composed of three kinds of regions, namely, G blocks with units derived from L-guluronic acid, followed by M blocks with D-mannuronic acid and the MG blocks comprising of alternating units of D-mannuronic acid and L-guluronic acid [27]. Different species of sea weed such as *Laminaria sp.*, *Macrocystis sp.*, and bacteria

like *Pseudomonas sp.* and *Azotobacter sp.* [28] are rich source of alginates. Polymer composition determines its physicochemical properties and the alginate composition, molecular weight, viscoelastic properties, and size polydispersity differ considerably depending on the source and growth environments. Bacterial alginates display diverse characteristics compared to algal alginates including acetylation, higher molecular weight, monodispersity, and different viscoelastic properties [29]. For commercial use, alginates are obtained from farmed brown seaweeds and are extensively used owing to their high biocompatibility and cell adhesion properties as viscoelastic regulators, stabilizer, and cosmetics applications and for high-value biomedical applications such as wound dressings and drug carrier systems. With the increase in molecular weight, alginate readily forms gels and this property of alginates is used for tissue engineering applications for developing alginate-based hydrogels as wound healing materials or drug delivery systems as they are nontoxic to biological systems. Injectable alginate hydrogels developed by Xiaojin Hao and colleagues was loaded with VEGF-A and with PDGF-BB showed sustained release and could be used as potential growth factor delivery system for treating myocardial infarction [30]. Similarly, various other growth factors like BMP-2, PDGF-BB, TGF- β , and antibiotics like gentamycin quercetin have been successfully delivered using alginate-based hydrogels for various bone, skin, and dental applications. Also, alginate-based nanoparticles and microparticles loaded with anti-cancer drugs like Doxorubicin, Docetaxel, cisplatin tested on different cancerous cell types have shown excellent anti-cancer activity indicating it to be a promising drug delivery system. Alginate can be easily reduced to form different types of nanoparticles and can be readily conjugated with various moieties making it suitable for various biomedical applications like bio-imaging. For cosmetic applications such as anti-acne, anti-aging formulation, alginate-based carriers have been explored. In vitro delivery of cedar wood essential, essential oils from thyme, clove, and cinnamon released from alginate microspheres showed excellent encapsulation minimizing the evaporation and antimicrobial activity make these microcapsules suitable for the cosmetics applications. In vivo studies on rats have explored the potentials of alginates as injectable fillers showing better capsule formation low adverse effects, suggesting a better long-term volumizing effect and minimal immunogenicity requiring further clinical validation to develop in to commercially available fillers.

3.2 *Fucoidan*

Fucoidan is a sulfated polysaccharide extensively found and isolated from the cell walls of several species of brown seaweed by multi-step hot acid extraction methods. It is primarily made up of sulfated fucose-rich groups and backbone composed of L-fucose units. The structure, composition, and bioactivity of fucoidan differ in sea weed species and type of extraction process [31]. Fucoidan is commonly isolated from *Fucales* and *Laminariales* but also in *Chordariales*, *Dictyotales*,

Dictyosiphonales, *Ectocarpales*, and *Scytosiphonales* species [32]. They show versatile biological activities like anti-inflammatory, immuno-modulatory, anti-tumor, and anti-coagulant activities [33], and these bioactivities depend on their structure, monosaccharide composition, sulfate content, and molecular weight [34]. Fucoidan is extensively explored in biomedical applications mainly focusing on tissue engineering, drug delivery, and biosensor application due to its biological activities. Fucoidan is negatively charged polysaccharide that readily forms polyelectrolyte complexes on combining with positively charged polymers. Thus different kinds of composites such as scaffold, hydrogels, nanoparticles, microsphere, etc., can be prepared for drug delivery applications. Fucoidan-based wound healing materials like injectable hydrogels and 3D scaffold loaded with growth factors imitate the extracellular matrix, allowing cell adhesion and proliferation promoting healing. Along with minimal cytotoxicity and non-inflammatory, it has been reported for antimicrobial activity against *Pseudomonas aeruginosa*, *Klebsiella pneumonia*, *Escherichia coli*, and *Staphylococcus aureus*. Fucoidan-based nanoparticles improved targeted delivery of doxorubicin, docetaxel, gentamycin enhancing anti-cancer activities. Cho et al., developed fucoiden-based theranostic nanogel for imaging as guided treatment of cancer. Manivasagan et al., and colleagues developed doxorubicin-loaded fucoidan capped gold nanoparticles with high efficacy and specificity for drug delivery and imaging applications [35–37].

Fucoidan is a rich source of both primary and secondary metabolites. Primary metabolites polysaccharides, proteins, amino acids, and fatty acids are key role players in development, growth, and reproduction while secondary metabolites such as phenolic compounds, pigments, and vitamins have direct significance in cosmetics applications. Studies report protective effects of fucoidan on hair and skin via free radical elimination, decreased inflammation, wrinkles, and allergies. Fucoidan isolated from *Fucus vesiculosus* with high polyphenol content showed good in vitro antioxidant activity and improved skin protection. The extract considerably reduced spots due to aging and increased skin brightness.

3.3 Starch

Starch is one of the most abundant polymeric carbohydrate made of 1, 4-linked D glucose units and is present in semi-crystalline form. They are heterogeneous and are classified into two principal forms, namely, amylose and amylopectin arranged in the concentric rings forming semi-crystalline and amorphous layers [38]. Amylose a linear form and contributes mainly to the amorphous segment of the starch while, amylopectin is a highly branched structure contributing to the peripheral crystalline arrangements of starch granules. Their ideal physicochemical characters make them suitable for various applications as gelling agents, stabilizers, coating materials, and moisturizers. These arrangements influence the thermal properties and mechanical strength. They are found in different types of plants are a rich source of energy.

Due to its low-cost, ease of accessibility, and biological properties, starch is extensively explored for biomedical research. Starch-based powder and film in applications such as tissue engineering and hemostatic application. Starch is widely used in solid dosage forms such as fillers, binder. They can be easily developed in to carriers for drug delivery with high encapsulation of the loaded drugs and modified starches are used as oral sustained release matrices and bio adhesives. Dorsa and lab mates developed Starch Micro/Nanoparticles loaded with curcumin with sustained curcumin release in vitro, to overcome curcumin hydrophobicity and instant degradation at physiological pH. Garima and colleagues developed starch-based thin films for delivery of antimigraine drug, zolmitriptan, and the formulated sago starch-based mucoadhesive oral films had excellent mechanical properties like elongation and tensile along with 96.45–99.43% of drug release in 6 hours from the films [39]. For cosmetic applications, corn, rice, and tapioca starch are explored for skincare and color cosmetics in the form of creams, lotions, body balm, and cleansing products. A peeling formulation in the form of spherical microparticles of sodium alginate and starch were synthesized using encapsulator BÜCHI B-395 Pro. The developed formulation enhanced hydration and the level of sebum without causing any skin irritation.

4 Biopolymers Derived from Microorganisms

Microorganisms produce polysaccharides that are cell-bound called the capsular polysaccharides and the ones secreted to the external environment referred to as the exopolysaccharides (EPS). These exopolysaccharides are sometimes synthesized by the enzymes anchored to the cell wall. EPS synthesizing ability has been found in microorganisms that belong to the domain Archaea and Bacteria. Based on their monomeric units they are classified as homopolysaccharides and heteropolysaccharides. Homopolysaccharides are composed of one type of monosaccharide unit, whereas the heteropolysaccharides contain different monosaccharide units [40]. The physicochemical properties of the EPS depend on factors like the host microorganism, environmental factors, isolation techniques, etc. The growth conditions like the medium composition, temperature, pH, and aeration determines the EPS composition, yield including the growth phase of the organism (see Fig. 3). These properties in turn determine the commercial application of these polymers. The EPS are known to exert benefits to the host like protection from environmental stress as in a hostile condition [41].

Few of the EPS producing bacteria are *Leuconostoc*, *Streptococcus*, *Weissella*, *Lactobacillus* sp.(dextran-producing) *Xanthomonas* sp., mainly *Xanthomonas campestris*, *Xanthomonas pelargonii*, *Xanthomonas phaseoli*, and *Xanthomonas malvacearum* (Xanthan gum-producing), *Sphingomonas paucimobilis*, formerly known as *Pseudomonas elodea* (gellan gum-producing), *Azotobacter* and *Pseudomonas* (alginate-producing), *Klebsiella pneumoniae* (fucogel-producing), *Clavibacter* strains (clavan-producing), *Streptococcus* (hyaluronic acid-producing),

Bacillus, *Zymomonas*, *Halomonas*, *Pseudomonas*, *Rahnella*, *Aerobacter*, *Erwinia*, *Streptococcus*, *Microbacterium* (levan-producing), *Sphingomonas* sp. (welan gum-producing) [40]. Some of the industrially significant EPS are dextran, xanthan gum, gellan gum, alginate, hyaluronic acid, pullulan, scleroglucan, fucogel, levan, schizophyllan, and welan gum [40].

4.1 Succinoglycan

Succinoglycan represents a major class of exopolysaccharides (EPS) like xanthan gum that are synthesized on undecaprenol carriers. It is a complex acidic exopolysaccharide chiefly composed of succinic acid and galactose residue. Succinic acid is primarily composed of several glucose residues. One galactose residue is present per seven glucose residues along with non-carbohydrate substituents like pyruvate, succinate, and acetate in succinoglycan [42]. Soil bacteria like *Agrobacterium tumefaciens*, *A. radiobacter*, *A. rhizogenes*, *Rhizobium radiobacter*, *Sinorhizobium meliloti*, *Ensifer meliloti*, and *Pseudomonas* sp. produce succinoglycan type of EPS with a yield up to 13.7 g/L.

Succinoglycans form oil-in-water type of emulsions and are known to possess thickening and plasticizing activity. This has made it a material of choice as a cosmetic additive [42]. The shear thinning, viscoelastic nature of succinoglycan obtained from *Rhizobium radiobacter* CAS and *R. radiobacter* ATCC 19,358 facilitates its use in cosmetics and drug delivery applications. In the presence of reducing agents, succinoglycans are known to enhance the drug release [43]. Addition of succinoglycan to agarose resulted in flexible and stable network gels in comparison with the hard and brittle agarose gel. This combinatorial hydrogel also showed pH-responsive delivery of ciprofloxacin [44].

4.2 Gellan Gum

Gellan gum is an anionic extracellular heteropolysaccharide produced by *Sphingomonas elodea*, *Sphingomonas paucimobilis*. It is composed of tetrasaccharide repeating units; 1,3-linked-D-glucose, 1,4-linked-D-glucuronic acid, 1,4-linked-D-glucose, and 1,4-linked-L-rhamnose in a straight chain [45]. It has the ability to form gel in the presence of metal cations and can be later processed into transparent gels that are heat-resistant. Gellan gum was first commercially used in Japan in 1988.

Gellan gum has gelling property that is dependent on temperature and pH. Floating beads containing gellan gum with incorporated clarithromycin prepared by ionotropic gelation were studied for stomach-specific sustained delivery clarithromycin to treat *Helicobacter pylori* infections. Gellan gum has been widely used as a disintegrating agent in oral drug delivery systems wherein the swelling behavior

and the concentration of gellan gum plays a major role. The in situ gellan gum-based system for the delivery of scopolamine hydrobromide through nasal route was found to decrease the symptoms of motion sickness in comparison with the other modes of administration. Due to their high biocompatibility, biodegradability, and injectability, gellan gum-based physical hydrogels are widely explored for tissue engineering applications.

4.3 Pullulan

Pullulan is a linear and neutral exopolysaccharide consisting of α -(1,6)-repeated maltotriose units via an α -(1,4) glycosidic bond produced by polymorphic fungus *Aureobasidium pullulans* (Coltelli 2020). Pullulan was first isolated and characterized by Bernier (1958) from *A. pullulans* culture broth. Other microorganisms that produce pullulan are *Tremellamesenterica*, *Cytariaharioti*, *Cytariadarwinii*, *Cryphonectriaparasitica*, *Teloschistesflavicans*, and *Rhodototulabacarum* [74]. Apart from the advantages common to other natural polysaccharides, pullulan exhibits good water solubility and water absorbing capacity. Also, it forms strong films and fibers that are transparent with excellent mechanical properties. The first commercially produced pullulan was marketed for the first time in 1959 by the Hayashibara Company in Okayama, Japan [46].

Pullulan in combination with other polysaccharides used as nonwoven tissue is able to load and release the necessary factors at various skin layers. In this way, it can be used as a smart skin care product or a dietary supplement that works against the fine lines, wrinkles, and black spots. The prebiotic property and inertness to mammalian amylases enables its use as an antioxidant and low-calorie dietary product. There has been work carried out on development of smart facial beauty mask and diet supplements with the help of nonwoven tissues and films using pullulan and nanochitinnanolignin complexes. According to the 2017 survey, the largest consumption of pullulan is observed in Japan (667 million tons), the second one being China (20.65%) and the USA being the third one (20.16%). Pharmaceutical industries contribute largely (40.74%) to the global consumption of pullulan, food industries account for the second one (36.24%). Research on this polymer shows that cosmetic industries could be the future market if novel formulations with pullulan are discovered [47]. Pullulan is a safe and effective biopolymer possessing unique properties like the water retention ability, gas barrier, and regenerative property that enables reconstruction of the extracellular matrix. The process of aging slows down certain skin growth and reproductive mechanisms including the innate surveillance which in turn influences regeneration [48–50]. The regenerative medicine helps in reconstruction of tissues wherein the role of innovative polysaccharides/biomaterials like pullulan, chitin, and nanolignin plays a beneficial role.

In order to re-establish the communication between the cells and keep the stratum corneum hydrated, there is a need for selective materials that can be released at right layer of the skin and interact with specific cells. This is also important to renew the

extracellular matrix of the dermis as in case of a disease or in old age. Here, pullulan composites that possess the ability of regeneration of healthy, wounded, and aged skin come to play.

4.4 Dextran

Dextran is a homopolysaccharide composed of α -(1,6) linkages and α -(1,2), α -(1,3), and α -(1,4) branch linkages and is obtained from the members of *Leuconostocaceae* like *Leuconostocmesenteroides* and *Streptococcus mutans*. Other bacterial genera like *Weissella*, *Pediococcus*, and *Lactobacillus* also synthesize sucrose by making use of a sucrose substrate. The unique properties of dextran that enables promotion of firmness of skin, radiance, and reduction of wrinkles makes it an ideal skin smoothing and brightening agent [51]. Dextran improves the blood flow and increases nitric oxide (NO) synthesis in human epidermal keratinocytes and hence exhibiting anti-inflammatory property [51].

Due to its very high encapsulation efficiency, monodispersity, biocompatibility, and low-cost chemical modification process, dextran finds application in drug delivery [52]. Dextran beads with entrapped protein was found to get subsequently released in a time-dependent manner in a study conducted by Mellors et al. [53]. Rubone encapsulated polyethyleneimine-poly (epsilon-caprolactone) micelles stabilized with anionic carboxymethyl dextran was efficiently delivered in HCC cells and could upregulate miR-34a expression thereby aiding in the treatment of hepatocellular carcinoma [54]. Carboxymethyl dextran and docetaxel, anti-cancer drug conjugates showed sustained release of the drug at physiological pH. An increased release rate was observed at $\text{pH} < 6.5$ as in case of intracellular environment. Dextran-rosmarinic acid conjugates was used to develop a polymeric antioxidant that can be used as a skin whitening agent.

4.5 Xanthan

Xanthan is an extracellular heteropolysaccharide that is made up of a cellulose backbone substituted with a charged trisaccharide chain containing pyruvic acid and acetate groups at every second glucose molecule [55]. It is produced by different species of the genus *Xanthomonas* a Gram-negative bacteria. *X. arboricola*, *X. axonopodis*, *X. campestris*, *X. citri*, *X. fragaria*, *X. gummisudans*, *X. juglandis*, *X. phaseoli*, and *X. vasculorum* are the important species that are mostly used in industries for large-scale production of xanthan gum. Xanthan has unique properties like increased solution viscosity at low concentration, the pseudoplastic nature, stability under varied pH, temperature, ionic strength, and under shear states [56].

Xanthan in combination with other polymers is used as supporting hydrogels and as excipient in tablets [56]. In a study conducted by Gilbert et al. [55], xanthan-based emulsions showed maximum stretchability when compared to the other polymeric emulsions. This is one among the texturing properties that characterizes a cosmetic product. Xanthan is widely used in cosmetic products as moisturizing agent, viscosity controller, and psychosensorial agent. A curcumin-loaded binary hydrogel containing xanthan and galactomannan showed their ability in the delivery of hydrophobic drugs [57]. Also, xanthan and galactomannan have conferred the hydrophilic matrix system for the controlled release of diclofenac sodium from capsules and tablets. Hydrogels with suitable stiffness can be prepared by mixing xanthan appropriately with polysaccharides like konjac gum, iota carrageenan, and kappa carrageenan.

Membranes containing xanthan and chitosan in the same mass ratio in the presence or absence of Pluronic F68 exhibited low cytotoxicity in vitro. The tensile strength was compatible with human skin and could absorb physiological fluids in large quantities. Hybrid biopolymer obtained by mixing natural–synthetic chitosan-glycidyl methacrylate, and xanthan gum supported the growth of fibroblasts. Hybrid scaffolds prepared using xanthan and magnetite nanoparticles provided conducive environment for the neuronal cell growth and differentiation in vitro.

4.6 Alginate

Alginate that is used commercially comes only from brown sea weeds (*Laminaria hyperborea*, *Ascophyllum nodosum*, and *Macrocystis pyrifera*). It is also secreted by bacteria like *Azotobacter vinelandii* and *Pseudomonas* sp. [44]. The isolation methods are not cumbersome and are cheap and it is eco-friendly. Apart from this, it is biocompatible, less toxic, shows good gelation ability in the presence of divalent cations, and this makes alginate to be widely used in pharmaceutical, cosmetics industries, and in biomedical field [58]. Also, it exhibits unique characteristics like sol–gel transition, provides inert aqueous environment, controllable porosity, and structural similarity to ECM. These properties make it an ideal biomaterial in tissue engineering and biomedical field [44]. Some of the major limitations of alginate are its poor tear strength due to which it has to be combined with other polymers, the depolymerization at higher temperatures that results in loss of viscosity and its inability to treat dry wounds [58]. Due to the lack of cell binding sites, alginate activates anchorage-dependent cell death and this can be overcome by modifying alginate with RGD peptides.

The alginate containing high amount of M component were reported to be evoke an immunological response that results in ten times more cytokine production when compared to G block containing alginates. In vivo studies conducted by Orive et al. [59] have shown that purification steps not only removed the impurities, it also avoided the antibody response in male Balb/c mice. Alginate derivatives like the amphiphilic derivatives synthesized using hydrophobic groups like alkyl chains

are known to form self-assembled structures like particles and gels in aqueous environment. These make them potential candidates for drug delivery applications [6].

In semi-dilute form, these derivatives showed steep shear thinning behavior and formed gel-like networks. These results were very much favorable for these alginate derivatives to be used in cartilage repair like synovial fluid viscosupplementation and in cartilage replacement. By using amphiphilic derivatives of sodium alginate, controlled release of loaded proteins was achieved by dissociating the physical hydrophobic network using surfactants. Sodium alginate that was hydrophobically modified using polybutyl methacrylate was found to exhibit prolonged drug release behavior compared to unmodified sodium alginate.

Sodium alginate does not possess mammalian cell adhesive sites naturally, specific ligands are necessary for them to initiate cellular interaction for application in tissue engineering [6]. Due to the abundance of integrin receptors that interact with the arginine–glycine–aspartic acid (RGD) sequence, these peptides have been chemically coupled to the alginate backbone.

Application of alginate in biomedical field is progressive as they are used in drug delivery and tissue engineering field due to their varied features. Alginate dressings are known to provide a moist environment in the wound area that helps in wound healing. Usually, alginate dressings are prepared by cross-linking alginate with calcium ions and further processing it to form freeze dried porous sheets (foam) and fibrous dressings. Alginate dressings absorb the fluid in the wound area to form gel that maintains the physiological moist environment in the wound site thereby minimizing the infection. It is also known to promote formation of granulation tissue and enhancing the process of epithelialization and hence healing [6].

4.7 Cellulose

Cellulose is the most abundant biopolymer on the planet and it is synthesized by bacteria, plants, and animals for varied biological functions [60]. Cellulose is made up of linear homopolysaccharide containing β -D-glucopyranose units linked by β -1,4 glycosidic bonds [61]. Some of the bacteria that are known to produce extracellular cellulose are *Sarcinaventriculi*, *Rhizobium*, *Salmonella*, *Azotobacter*, *Achromobacter*, *Agrobacterium*, *Alcaligenes*, *Pseudomonas*, *Acetobacter*, and *Gluconacetobacterxylinus* [62]. Bacterial cellulose is the biopolymer of interest for tissue engineering and pharmaceutical applications when compared to plant-derived cellulose. This is due to the unique biological properties of bacterial cellulose like biodegradability, hydrophilicity, biocompatibility, and its ability to integrate with nanoparticles. The easier degradability of bacterial cellulose in comparison with the plant cellulose is due to its fibrous microstructure and high degree of crystallinity.

The biocompatibility of the bacterial cellulose hydrogel was improved by incorporating different extracellular matrices like collagen, elastin, and hyaluronan and certain growth factors like human basic fibroblast growth factor (B-FGF), human epidermal growth factor (H-EGF), and keratinocyte growth factor (KGF) [63]. Studies have shown that bacterial cellulose has good antibacterial activity that was profoundly increased when used as a combination with other antimicrobials with bacterial killing in a controlled manner and maintenance of a moist wound environment that facilitates its use in the treatment of wounds. Foundation liquid prepared using hemp/cellulose nanocrystals possessed good concealing feature, easy-wiping property that resolves the post-makeup skin cleaning problems has been prepared by He et al. [64].

Cellulose nanofibrils find their application in drug delivery due to the presence of relatively reactive surface, flexibility, elasticity, lower density, and lower toxicity. The cellulose materials when used as enteric coatings on capsules improved acid resistance in the stomach. For topical and transdermal drug delivery system, cellulose acetate-based drug-loaded nanofibers are significantly gaining attention due to their regenerative properties, high modulus, flexural, and tensile strength (Table 1).

Table 1 The major products developed from biopolymers and their chemical composition

Biopolymer	Chemical composition	References
Rose soothing hydrogel mask	Sodium polyacrylate, glycerine, cellulose gum, water	Aswathy [65]
Kelcogel [®]	Gellan gum	Matricardi [66]
AlgiSite [™] (Smith & Nephew)	Calcium alginate	McBride [67]
ComfeelPlus [™] (Coloplast)	Sodium carboxymethylcellulose, calcium alginate	Goodhead [68]
Purilon [®]	Calcium alginate, sodium carboxymethyl cellulose	Aswathy [65]
Kaltostat [™] (ConvaTec)	Sodium alginate	Baichwall [69]
Sorbsan [™] (UDL Laboratories)	Sodium alginate	Frankal [70] and Portela [71]
Tegagen [™] (3 M Healthcare)	Xanthan	Aderibigbe and Buyana [4]
TIMERx [®]	Xanthan	Staniforth [72]
SOLOSITE [◇] Gel	Sodium salt of carboxymethyl cellulose and glycerol	Aswathy [65]
XCell [®]	Cellulose	Del Valle [73]
BioProcess [®]	Cellulose	Portela [71]
Gengiflex [®]	Cellulose	Portela [71]

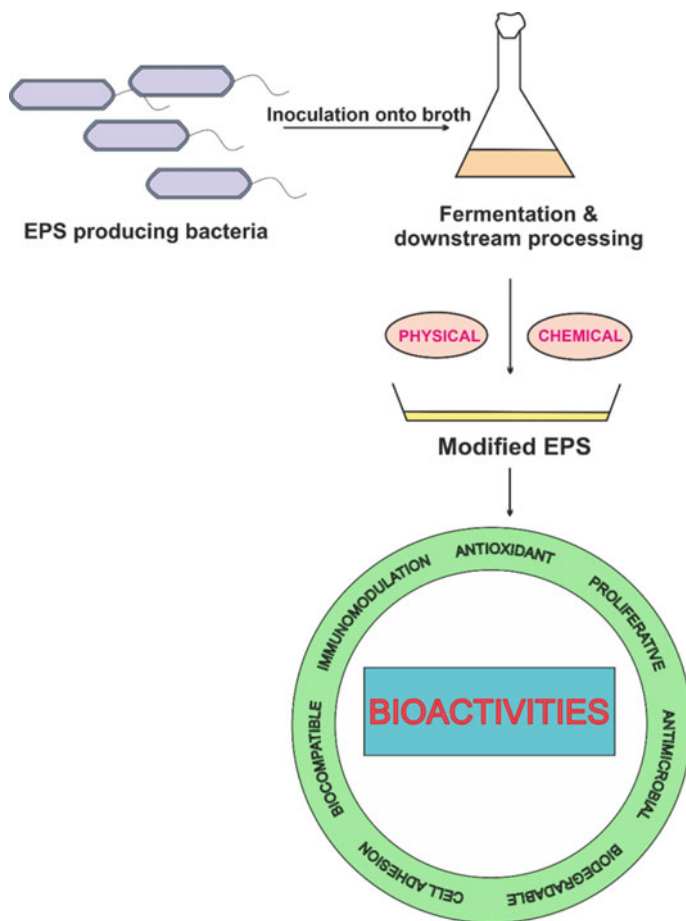


Fig. 3 Schematic representation of isolation and ideal properties of exopolysaccharides that enables its biological applications

5 Conclusion

Biopolymer-based materials have proven to be innovative approaches for biomedical, pharmaceutical, and cosmetic applications. As most of the biopolymers have ideal physicochemical properties and biocompatibility, further progress has been made by several modifications to enhance their functions as suitable materials for drug delivery, wound healing, anti-cancer therapies, adhesives, stabilizers, moisturizers, etc. Most of the developed materials have been tested on various *in vitro* and *in vivo* models with desired outcomes and need further clinical validation for developing into commercial products.

This has been a growing field of research for both industries and academia and among various biopolymers, majority of the biopolymers have found many applications in the biomedicine and cosmetic applications. For example, in drug delivery systems, such as nanoparticles, scaffolds, or hydrogels fabricated from biopolymers ensure high drug encapsulation with steady release for targeting various disease models. While few other biopolymers due to their high viscosity, water holding capacity, and biocompatibility are used for skin, hair, and dental care applications. They can be easily isolated from various natural sources, readily modified into desirable forms based on the application and is economic, making biopolymers an ideal and potential choice.

Although there has been extensive research conducted that proves the bioactivities of the polymers, only a handful of them have reached the stage of clinical trial and are marketed. This lacuna in transforming these novel molecules into a commercial product is possible when related research and the outcomes are well studied. This chapter is likely to pave way towards improvising the biopolymer-based materials for commercial-scale production.

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Biopolymers in the Leather Industry



Ana Maria Mazotto

Abstract Leather is a material extensively used for producing apparel, accessories, furniture, and upholsteries. However, the conversion of hides into leather consumes a large quantity of water, hazardous chemicals, and generates problematic waste. Several approaches have been explored to improve sustainability in leather processing in the last few years. Thus, biopolymers as raw material for leather-like materials or in the tanning process to reduce the use of chromium and other toxic compounds have arisen as an efficient solution. Structural and abundant biopolymer as cellulose from both plant and bacterial sources can be used as raw material for leather products or in the leather process as tanning, retanning, and finishing. Proteic polymers such as collagen, fibroin, and keratin offer possibilities for designing new composites with the same application as natural leather. Biomass derived polyaldehydes have been investigated as a tanning agent to substitute chrome tanning. Chitosan can be used as a tanning agent and an antimicrobial coat to preserve leather, especially footwear leather. Collagen extracted from scraps or trimmings waste or soy hydrolyzed can be applied in retanning, and pectin can be a component of the fatliquor agent. In this chapter, the multiple applications of biopolymers in the leather industry are presented.

Keywords Biopolymers · Leather · Tanning · Collagen · Cellulose · Polyaldehyde

1 Introduction

Since ancient periods, humans have been using leather. This material is used in apparel, upholsteries, furniture, and accessories due to its malleability, warmth, flexibility, resistance, impermeability, and higher aesthetic and rich look. Due to its compatibility with mechanical and chemical treatments, leather is appropriate for

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large-scale industrial manufacturing. However, the conversion of hides into leather consumes a large amount of water, hazardous chemicals and produces complex solid and liquid wastes [1]. To produce a pair of leather boots is required 50.2 m² of land and 14,500–25,000 L of water beyond 30 lb of carbon dioxide emitted to the environment [2, 3].

There has been an increasing concern about fashion environmental impact, especially for the high use of energy, water, and chemical products. The fashion industry accounts for 20% of water pollution and, among all effluents, tannery effluents are among the most worrisome due to the large number of toxic chemicals used in the processing of animal skins [4, 5]. Leather industries are one of the most dangerous producers of toxic effluents per unit of production. Depending on the process adopted and the type of skins utilized, the pollution level caused can differ among the industries. The harmful chemicals include wetting agents, formic acid, ammonium sulfide, sodium sulfite, sodium chloride, sodium arsenite, sulphuric acid, hydrochloric acid, ammonium chloride, caustic soda, soda ash, calcium oxide, and chromium oxide. These chemicals are responsible for the complexity of tannery effluent treatment using conventional wastewater treatment technologies [4]. The existence of chromium in the effluent is a significant threat to the environment once chromium compounds is highly toxic [6]. Additionally, air pollution with hydrogen sulfide is a severe health problem in tannery areas [7].

The discarding of the tannery waste into soil and groundwaters without appropriate treatment affects soil productivity. It negatively impacts the environment and causes health disorders such as respiratory and renal issues, skin disease, diarrhea, cancer, and dizziness [8]. The tannery wastewater affects important economic sectors, decreasing agriculture productivity and compromising the health of livestock and fish.

Several tactics have been explored to improve the sustainability in the leather processing industry in the last years pressed by consumers and governments to minimize adverse environmental impacts, reduce energetic and natural resources, and improve the safety of employees, communities, and consumers. The importance of sustainability became solidified by the United Nations in 2015 when the 17 Sustainable Development Goals (SDGs) were defined [9].

There are many approaches for reducing the impact of this industry, but the one that has shown the most significant potential is the replacement of the raw material used in production with biopolymers. In this way, the entire process is redesigned to use non-toxic chemicals and less water. The substitution of tanning agents, the main chemical compounds that cause deleterious effects, with biopolymers capable of stabilizing collagen has also shown excellent results. As presented throughout this chapter, a vital alternative to improve sustainability in the leather industry relies on biopolymers.

2 Overview of Tannery Process

Tanning is the procedure of transforming raw animal skin or animal hides through several chemical and physical treatments to produce a more robust material, useful for several applications [4, 3]. The first step of leather manufacture is handling the animal skins to prepare the rawhide. About 8–9 million tons of fresh animal hides are produced per year. A large portion of the leather production happens predominantly in developing nations, especially in Asia. China is regarded as the highest producer (25%), followed by Brazil (9.5%), Russia (7%), India (6.4%), Italy (6.3%), and South Korea (4.8%) [10].

The skins or hides used for leather production come from slaughterhouses; thereby, the tanneries reduce their disposal through the use of the skin, a non-edible part of the animal [4]. However, the conversion of hides in leather produces liquid, solid, and gaseous toxic wastes more environmentally harmful than the disposal of skins.

The chain begins in the slaughterhouses, where animals are slaughtered, and their hides and skins are collected and usually salted. The next step occurs in the tannery, where the salted or unsalted hides and skins are converted into leather through three main processes: pre-tanning, tanning, and post-tanning [4, 9] (see Table 1).

In the pre-tanning process, the hides are soaked in water for fleshing and unhairing. To prepare the hide for tanning, the skins are treated with lime and several other chemical compounds to remove their hair. The subsequent step is the tanning process. This process consists in removing unnecessary proteinaceous matter and stabilizing the collagen matrix of the hides. There are three main types of tanning: vegetable tanning (treatment with polyphenolic compounds), chrome tanning (treatment with chromium), and combined tanning. About 85–90% of the leather industrially produced worldwide uses chrome tanning [1].

The skin structure is partially degraded during the tanning process to facilitate penetration and fixation of chemicals (tanning agents) that stabilize collagen structure [1]. Numerous toxic substances such as chromium, zirconium, formaldehyde, oils (such as short chain chlorinated paraffin), silica, Calgon, and aluminum are used in this step [4]. Reduced chromium present in the slurries (Cr(III)) may be oxidized to Cr(VI) species that are toxic and harmful. Cr(VI) species are the most worrying pollutant of the effluents of the leather industry. Besides, oils are also used in the tanning process. The oils present in tannery wastewater are harsh to degrade [4].

The final step is the finishing process, where the tanned hides are often retanned to acquire some desirable textures and properties. Further, the tanned skin is bleached or dyed, and lubricants are applied according to the desired final product. Thus, several pigments, waxes, resins, fillers, and binders are utilized in this process step. Among the hazardous compounds used are phthalates as plasticizers agents, nonylphenol, biocides, and N-methyl pyrrolidone. The last one provides high-performance leather but is identified as a reproductive toxin [4, 3].

Even with all leather production issues, consumers value leather [1]. The demand for leather products is increasing, driven by fast fashion. Product life cycles in fast

Table 1 Leather production overview

Process	Descriptions	Waste ^a
Pre-tanning	Preservation: treatment to protect the skin from decomposition	Fleshing BOD
	Soaking: washing or hydration of the skin with water	COD SS
	Liming: elimination of undesirable protein	Salts
	Unhairing: elimination of animal hair from the skin	NH ₃
	Fleshing: removal of subcutaneous material	SH ₂
	Splitting: cutting of skins into two or more horizontal layers	
	Reliming: further elimination of protein and opening-up process	
	Deliming: removal of liming and unhairing chemicals from the skin	
	Bating: removal of proteins using proteolytic proteins and softening process	
	Degreasing: removal of natural fats, oils, and grease from the skin/hide	
	Frizing: physical removal of fat layer inside the skin	
	Bleaching: chemical modification of darker pigmented skins into light-colored pelt	
	Pickling: lowering of pH value to the acidic region	
	Depickling: increasing pH	
Main tanning	Chrome tanning, vegetable tanning, or combined tanning: chemical reactions to convert skin into leather, making it more durable and less susceptible to decomposition	BOD COD SS
	Sammying: removal of excess moisture from a hide through pressure applied by rollers	Salts Chromium
	Sorting: quality check to sort according to the quality	
	Splitting: the hide/skin is cut into two or more horizontal layers to get a uniform thickness	
	Shaving: thinning and equalizing using a leather shaving machine that cuts off leather fibers from the flesh side	
Wet finishing	Neutralizing: leftover acids from the tanning are neutralized	Trimmings
	Retanning: modify the physical characteristics of the leather to suit its final use	BOD COD, Chromium
	Dyeing: adding color to the leather	Dye Fat
	Fatliquoring: reapplying water-soluble oils to leather	
	Setting: the leather is stretched out and the grain side is smoothed	
	Drying: removal of water to 10–20% water contents	

(continued)

Table 1 (continued)

Process	Descriptions	Waste ^a
Finishing	Buffing and brushing: the flesh surface is removed by mechanical abrasion to produce a suede effect or to reduce the thickness	Solid residues Liquid residues Solvents Formaldehyde
	Conditioning: adding moisture to the leather	
	Pigmentation: adding color to the leather	
	Trimming	
	Protein binders, thermoplastic finishes, and nitrocellulose finishes: adjust gloss level	
	Final grading: grading may consider the color intensity and uniformity, the feel of the leather, softness, visual appearance, thickness, design effects, and natural defects such as scratches	

<http://www.fao.org/3/X6114E/x6114e05.htm#TopOfPage>; https://www.leather-dictionary.com/index.php/The_Leather_Dictionary, both accessed on November 3rd, 2021

^aOnly 270 kg of leather is produced from 1000 kg of rawhides. The process generates 730 kg of solid waste [11]. Out of 1000 kg of rawhides salted, 452 kg of chemicals are added, and only 15% are retained to obtain finished leather [12]

fashion are getting shorter, motivating the consumers to purchase new items in a short time. Fast fashion is characterized by the rapid obsolescence of goods [13]. Leather production is expected to grow approximately 3% CAGR and to reach about US\$ 86.3 billion by the end of 2027. However, the number of consumers worried about environmental issues is crescent and refrains from purchasing products made from traditional leather [14]. Sustaining this new demand and reducing the footprint of conventional leather production require different approaches to producing sustainable leather or new materials. Material choice is one of the crucial solutions for increasing the leather industry's sustainability and reducing the harmful environmental impacts.

3 Alternatives for Animal-Based Leather Using Biopolymer

The increased spotlight on animal rights and the stringency of laws regulating leather manufacturers are propelling demand for synthetic substitutes [2]. Consumers who avoid buying animal-based leather prefer polyurethane (PU) or polyvinyl chloride (PVC) leather, or other alternatives. These synthetic leathers are not considered sustainable [15]. An advantage of these alternative materials is their high abundance and lower cost than animal leather. The global synthetic leather market has been growing, driven by footwear, automotive, and furnishing industries. Although the Higg Index of synthetic leather is lower than conventionally processed leather, synthetic alternatives also produce toxic load on the environment, use non-renewable raw sources, and are non-biodegradable [1]. Therefore, new leather substitutes are

needed. As a consequence of the growing ecological awareness, many large companies such as H&M, Land Rover, Tesla, Adidas, Puma, and Nike are developing eco-friendly leather from alternative sources.

3.1 *Leather from Cellulose Sources*

Cellulose is the polymeric carbohydrate most abundant, inexpensive, and available globally. It is commonly extracted from plants or their wastes once cellulose constitutes the primary plant cell wall structure. Cellulose biopolymer is a polysaccharide formed by linear chains of D-glucose units linked by $\beta(1 \rightarrow 4)$ linkages (Fig. 1). Traditional textiles such as cotton and linen are cellulosic fibers. Cotton is the second fiber most consumed after polyester, with a production of approximately 27 Mt per year [16]. There are several concerns about cotton cultivation. The cotton crops consume approximately 25% and 11% of globally produced insecticides and pesticides, respectively [17]. These chemicals can promote damages to human health and environmental problems such as water and air pollution, insect and weed resistance, exhausted soils, and loss of diversity. Additionally, cotton crops consume a large volume of water: 7000–29,000 L of water is necessary to produce 1 kg of cotton fiber [18]. This amount is enough fiber to produce only one pair of jeans [17].

Traditional cellulose sources used in the textile industry are not the best choice for sustainable leather production. However, cellulose has properties interesting for leather-like products. Thus, several new cellulosic materials have been developed to increase the sustainability of the leather industry. As we will see below, many of these fibers have molecular arrangements and physical and chemical properties that make them promising substitutes for animal leather.

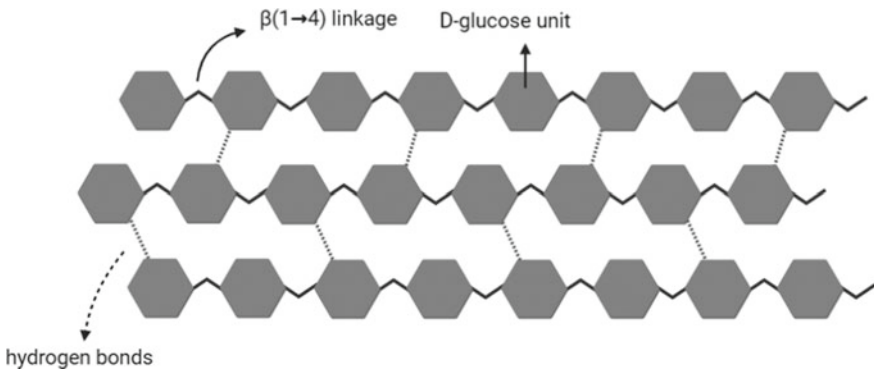


Fig. 1 Cellulose structure. Polysaccharide strands stabilized by hydrogen bonds (created with [Bio Render.com](#))

3.1.1 Bacterial Cellulose-Based Biopolymer for Leather Production

Although plants are the primary provider of cellulose, various bacteria can produce cellulose. Classically, Bacterial Cellulose (BC) is synthesized by bacteria of *Komataeibacter* genus as *K. xylinus* (formerly *Gluconobacter xylinus*), *K. hansenii*, *K. kombuchae*, and *K. intermedius*, *K. sucrofermentans*, and *K. medellinensis* [19, 20, 21]. However, other bacteria have been reported as cellulose producers, such as *Gluconobacter cerinus*, *Enterobacter amnigenus* GH-1, *Acetobacter aceti*, *Acetobacter okinawensis*, and some bacteria of *Bacillus* genus as *B. megaterium* and *B. aryabhatai* [22, 23]. The exploration of diverse bacteria strains is justified by the different properties of celluloses from different sources, presenting distinct possibilities of applications [24].

Bacterial cellulose (BC) was first reported by Brown in 1886, who observed the growth of bacteria on the surface of the medium forming a pellicle with a structure chemically equivalent to plant cellulose [25, 26]. The molecular formula of BC and plant cellulose is the same ($C_6H_{10}O_5$)_n. The cellulose macromolecules are structured in an unbranched D-glucose chain 4-β-glycosidic linked in a linear form. However, BC is chemically pure, while plant cellulose is found together with lignin, hemicellulose, wax, or pectin. So BC does not necessitate extra processing to remove impurities [21]. Due to the purity of BC, it exhibits numerous physical and chemical features such as unique nanostructure, high water-absorbing capacity, insoluble in most of the solvents, high degree of polymerization (up to 800), high mechanical strength, high crystallinity (of 70%–80%), and ultrathin structure [25, 27, 28]. It is flexible, biocompatible, and over ten times stronger than plant cellulose [2]. Besides, BC is formed by abundant hydroxyl groups, allowing for more straightforward chemical modification [29].

BC is formed by subfibrils of 1.5 nm comprised of β-1 → 4 glucan chains connected by inter- and intra-hydrogen bonding assembled into nanofibrils of 2–4 nm width usually (reaching up to 25 nm), composed of 10–250 single polymeric chains, organized into microfibrils of 40–60 nm width [30, 25, 21] (Fig. 2). Compared

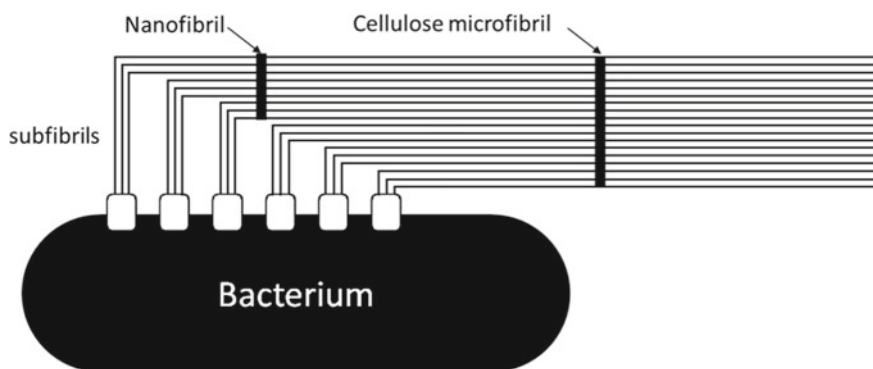


Fig. 2 Model of assembly of cellulose microfibrils described by Cacicedo et al. [30]

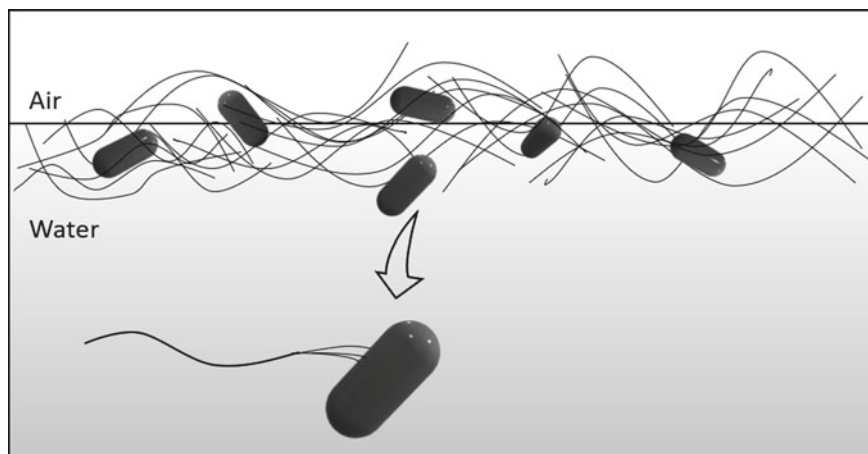


Fig. 3 Schematic representation of the bacterial cellulose network formation under static condition fermentation (modified from Rühls et al. [32])

with microfibrils of plant cellulose, BC microfibrils are 100 times smaller [31]. The BC nanofibril structure is answerable for the high tensile strength, the high degree of polymerization, and crystallinity [21]. The nanofibrils are arranged in a web-shaped network structure, forming a porous matrix (Fig. 3). The fibrous network is a three-dimensional structure with nanofibers well-arranged and highly interwoven, resulting in porous hydrogel sheets with high surface area [25, 32, 28].

The production of BC is an aerobic process conducted in static (surface growth), agitated, or stirred conditions in a medium containing glucose or other saccharides as a carbon source. Depending on fermentation conditions, different structures of cellulose are produced. Under the static production, a three-dimensional reticular pellicle is formed in the air–liquid interface [25, 32], while in agitated or stirred conditions, irregular sphere-like cellulose particles (SCP) are produced [33]. The static state has been used in large trays for textile to obtain the cellulose pellicle [34]. The thickness of the pellicle can be controlled through the cultivation time, longer cultivation time produces thicker pellicles. Synthesis of bacterial cellulose reaches its limit when the pellicle sinks and submerges all bacteria, inactivating them by insufficient oxygen supply [35]. Comparing static production and agitated conditions, the first one has a lower yield. However, the SCP formed through agitated fermentation has lower crystallinity, mechanical strength, and polymerization degree [25], probably due to the effects of aeration and shear.

The BC production also depends on the carbon and nitrogen sources used in the culture medium [36]. Carbon is the essential nutrient source for bacterial cellulose production. The primary carbon used for the production is sugars and derivatives such as sucrose, glucose, and fructose. Nitrogen sources also sustain bacterial growth and production, and the addition needs to be considered. The nitrogen sources usually used in bacterial cellulose production are peptone, yeast extract, ammonium sulfate,

glycine, and casein hydrolysate [3]. The optimization of carbon and nitrogen concentrations and the use of alternative sources as agricultural waste can reduce production costs [37, 38]. The most well-known BC used as textile material is produced in static fermentation of black or green tea broth with sucrose (5–8%), using a symbiotic consortium of bacteria and yeast popularly known as “SCOBY.” During the growth on the tea surface, the SCOBY forms cellulosic pellicles utilized as fabric [39, 40]. This fermented tea is also named kombucha, a probiotic brewing.

After the growth of cellulose bacterium producer, either in pure culture or in a consortium, the pellicles formed in the top of the culture medium by the accumulation of cellulose microfibrils are dried to produce a resilient material that resembles leather, with similar properties of finely finished leather. These properties include softness and elasticity. BC is comparable to the leather used in the footwear industry but could also be employed in the automotive, clothing, and furniture industries [2]. The physical properties and appearance of BC are responsible for its success in the leather industry as an alternative material. The first designer to popularize the BC as a leather-like material was Suzanne Lee. She founded the design consultancy “BioCouture,” which produces bio-based fabrics from living bacterial species [41]. Nowadays, several researchers have been developing BC materials for fashion applications. Other teas and even coconut water and wastewater of soybean fermentation from tofu production had been used to produce BC material as leather-like material with different properties [3].

Although BC is sustainable and easy to produce, several drawbacks need to be overcome, so various modified methods have been reported. For example, the cellulose sheet, after drying, may lose its flexibility, which can be solved by adding different plasticizers [42]. For footwear purposes, hydrophobicity is required, so BC can be combined with another polymer to produce anti-wetting and self-cleaning materials [43], treated with fabric softener [44], or even functionalized with therapeutic compounds such as antimicrobial and antioxidants agents, and with skincare products for the cosmetic purpose [2].

The two main strategies for BC modification are biosynthetic (in situ) and ex-situ methods [45]. In the biosynthetic (in situ) process, BC is modified during bacterial cell growth by adjusting the culture conditions and inserting supplementary materials into the culture medium. An example of an in situ growth process is the addition of polyvinyl alcohol (PVA). [46] produced bio-nano-composites prepared by the direct addition of PVA into *Acetobacter xylinum* culture. The PVA acts as a plasticizer disrupting hydrogen bonding between cellulose fibrils within the BC network. PVA-BC sheet was compared to pure BC sheet, and the bio-nano-composite had lower Young’s modulus and higher toughness [46].

In the ex situ modification, previously produced BC is chemically treated by acetylation, graft copolymerization, or/and crosslinking reaction to modify its chemical composition and combine BC with other materials such as plasticizer polymers or active agents [45]. For instance, [47] incorporate two different plasticizers individually (glycerol and polyethylene glycol) into dry BC previously prepared. Plasticized dry BC membranes showed higher elongation at break, water absorption, and a water

retention rate [47]. Ex situ modification also includes physical treatments to change porosity, crystallinity, and fiber density [28].

The advantages of BC leather over animal and artificial leather are

- The production method based on biological processes is more sustainable than the leather manufacturing process. Even if BC had a small market share of the leather industry, it could reduce the demand for animal hides, greenhouse gas emissions, and toxicity associated with tanning.
- BC production does not require toxic chemicals.
- BC is biodegradable and can be disposed of safely.
- BC does not cause allergic reactions.
- BC can be used in a printable fluid to produce 3D print garments.
- The production requires a much lower land space as compared with land suitable for stock raising.

Besides many studies at the laboratory level and many technical applications for bacterial cellulose, few BC-based products are commercialized today. The challenges to overcome for commercial implementation of BC are

- The necessity of reducing water absorption and wettability properties. To overcome these properties, BC needs surface modification to become hydrophobic for application as a leather alternative. So, studies to improve the intrinsic incompatibility between cellulose and hydrophobic polymer needs to be performed [48].
- The commercial production of BC is limited by the high production cost and the low yield. The cost of culture medium contributes to 40% of total process cost, so economic viability should be investigated in medium development and optimization conditions to the economically viable fermentation.
- Bacterial cellulose films tend to lose water, which could collapse the structure, causing loss of texture, tensile strength, and other comfort and aesthetic properties.
- The quality of BC produced is hard to reproduce in all batches, needing efforts to solve the problems of process standardization.
- The production process is aerobic; therefore, the reactor's design is a crucial research field to improve the yield and quality of BC in static cultures where the oxygen transfer rate is limited.
- Genetically modified strains can be developed to improve the BC structural characteristics and productivity.

3.1.2 Vegetal Cellulose-Based Biopolymer for Leather Production

Leather and fur symbolize luxury for consumers for a long time. However, a popular opinion about animal garments has changed by increasing conscience about the cruelty of mass livestock and hunting and the unsustainable leather production process that emitted toxic chemicals [49]. Recent market research found that 37% and 23% of people in the UK and the US, respectively, think leather is inappropriate for clothing use [50]. This consumer trend has led major brands to ban the use of

exotic animal skins and support the development of more eco-friendly materials. That has motivated several independent designers and startups focused on material development to search for new alternatives for traditional leather or petroleum-based plastics PU or PVC, commonly used in synthetic leather [49]. As seen in the previous session, cellulose is a biopolymer that can be converted to materials with characteristics that resemble leather. In this way, diverse initiatives have used plants as a raw material to produce “vegetable leather.” Table 2 summarizes the currently available leather.

One of the most popular vegetable cellulose leather is Piñatex, a leather-like material developed by Carmen Hijosa, a leather industry consultant. This new leather is made from pineapple leaf fibers with the addition of thermoplastic polyester and petroleum-based resin. About 80% of Pinatex leather comprises pineapple leaf fibers, and the remaining 20% are polylactic acid fibers. It is estimated that 85–90% of

Table 2 Examples of vegetal cellulose-based leathers

Vegetable	Product	Company/startup/designer	Link
Pineapple leaves	Piñatex	Ananas Anam	https://www.ananas-anam.com/ ^a
Nopal cactus leaves	Cactus leather	Desserto	https://desserto.com.mx/home ^a
Areca palm leaves	Palmleather	Tjeerd Veenhoven	https://www.tjeerdveenhoven.com/portfolio_page/palm-leather/ ^a
Wood fibers	Lino leather	Don Kwaning	https://www.donyawkwaning.com/linoleather ^a
Coffee (recycled coffee, coffee beans, and coffee plant)	Coffee leather	nat-2	https://nat-2.eu/collections/nat-2-coffee-line/ ^a
Grapes (skins, stalks, and seeds of grapes)	Grape leather	Vegea	https://www.vegeacompany.com/ ^a
Apples (waste from apple juice production)	Apple leather	Happy genie	https://happy-genie.com/pages/materials ^a
Leftover mangoes	Mango leather	Fruitleather Rotterdam	https://fruitleather.nl/ ^a
Pulp of mulberry tree leaves	MulbTex	Gunas	https://www.gunasthebrand.com/pages/manufacturing-materials ^a
Corn pulp	Corn-leather	Benevolo	https://benevolo.com.au/pages/corn-leather ^a

^aAccessed on November 3rd, 2021

Pinatex is biodegradable, and 10–15%, which corresponds to the coating material, is not biodegradable. The production processes begin with the fiber extraction of pineapple leaves through decortication. The long fibers obtained are washed, dried, and degummed. The next step is meshing, where the fibers are turned into a cotton-like material converted into a felt-like sheet or a non-woven mesh structure. These sheets are transformed into leather alternatives through a treatment process with resins. In the finishing process, the pineapple leather is dyed, treated to get the desired look and feel, and coated to gain a protective surface to improve the water and abrasion resistance. Pineapple leather is heat-resistant, impermeable, flexible, soft, durable, and breathable, having some properties related to natural leather and others similar to synthetic leather [1, <https://www.ananas-anam.com/>, accessed of November 3rd, 2021].

Pinatex is more expensive than synthetic leather but less expensive than some natural leather. While most cellulosic leather is yet in the prototype phase, Pinatex has been commercialized by Hugo Boss, H&M, and Canadian brand Native Shoes.

Using fibers of leaves as Pinatex, some other plant-based leather has been produced, for instance, the leather developed by Tjeerd Veenhoven, the Palmleather. This leather is made from fibers of dry and brittle leave from the Areca Betel Nut. Another example is the Lino leather made from linseed oil, wood fibers, pine resin, limestone, and lignin, a composition adapted from linoleum. Pulp and peel of apples from the fruit juice and compote industry have been used to produce leather. In the production of Apple Skin, apple waste is converted into a powder blended with polyurethane (50% of apple residues and 50% of PU) and used to coat a cotton and polyester canvas. Apple leather is a durable, respirable, and soft material suitable for accessories manufacturing. Several other examples of leather made from plants are in Table 2.

3.2 *Alternative Protein-Based Leather*

3.2.1 *Leather from Collagen Source*

Collagen is the most abundant structural protein in vertebrates and invertebrates, corresponding to nearly 30% of the total proteins of an animal. This protein is present in connective tissues, including skin, bone, vascular systems, intramuscular connective tissues, and tendons, acting in the structural integrity and stability of the corresponding tissues and organs [51, 52]. The collagen molecule is formed by three α -chain proteins, with approximately 1,000 amino acids, about 100 kDa, and high glycine content [51]. According to the collagen types and sources, the trimer may be composed of a homotrimer or a heterotrimer. For instance, type I collagen is frequently a heterotrimer, with two identical α_1 -chains and one α_2 -chain. The ability of type I collagen to produce insoluble fibers with high tensile strength and stability *in vitro* was exploited to produce leather.

The first step of collagen biosynthesis is the translation of genes that codify specific α -chain genes. The protein undergoes post-translational hydroxylation and glycosylation, so a heterologous expression system needs to realize post-translational modification for biosynthetic production. A critical post-translational modification is the hydroxylation of proline residues in the Yaa collagen sequence that significantly increases triple helices' thermal stability. The amino acid sequence and composition of collagen monomers allow for tight packaging of three helical α -chains to form the final superhelix so that the core contains the hydrophobic amino acid residues. For this packing of helices, the third residue of the primary structure is glycine, present in the repeated XaaYaaGly sequence. Proline is the amino acid most frequently found in the Xaa position (28%), and the Yaa positions are often occupied by hydroxyproline (38%) [53]. The superhelical structure is reinforced by conformational constraints and hydrogen bonds between hydroxyl groups of hydroxyprolines [51].

Each collagen chain is capped by the telopeptide, short peptide extension without the XaaYaaGly sequence at the end of the molecule. The telopeptide domain is responsible for stabilizing the typical fibril assembly once it determines the intermolecular interactions. The telopeptide amino acid sequence may differ between species, whereas certain regions involved in crosslinking to form fibril are highly conserved [51]. After procollagen triple helix secretion into the extracellular matrix, the molecules have the N- and C-terminal propeptide cut off by specific peptidases and self-assemble to form striated fibrils aligned head to tail in a staggering quarter assortment. Consequently, the crosslinking sites of different collagen molecules are close enough to allow crosslinking at the telopeptide. Matured collagen is extensively crosslinked and usually insoluble in water. Collagen with fewer crosslinks is generally present in young tissues being soluble in water and acid [54].

Hydrogen bonds and other non-covalent interactions carry out the stabilization of the collagen triple helix. The alignment of charged groups promotes the hydrophobic and electrostatic interactions between collagen monomers and contributes to the fibril stabilization and quarter-staggered agreement. In the skin, collagen fibrils are randomly oriented in a two-dimensional network exhibiting mechanical strength in the network plane (Fig. 4) [54].

The collagen family has at least 28 distinct collagen proteins coded by 45 genes which form collagen types with different sequences, structures, and functions. Collagens may be classified according to their superstructural organization. The fibril-forming collagens are the major types of collagen present in skin, tendon, and bones (type I collagen), cartilage (type II collagen), and skin and vasculature (type III collagen). These collagen types are essential for tissue architecture and integrity. Due to the self-assembly of type I collagen in fibrillar structures, it can be used for numerous purposes [51, 54]. Collagen extracted from animal tissues such as bovine or porcine skin and scales of fresh water and marine fishes finds biomedical applications in reconstructive medicine [55].

Collagen can form film and three-dimensional structures. To form thin films, a collagen solution can be processed by casting. To produce three-dimensional scaffolds, methods as 3D printing freeze-drying, gas-forming foam, electrospinning, thermal-induced phase separation, and the precipitation of crystals can be used.

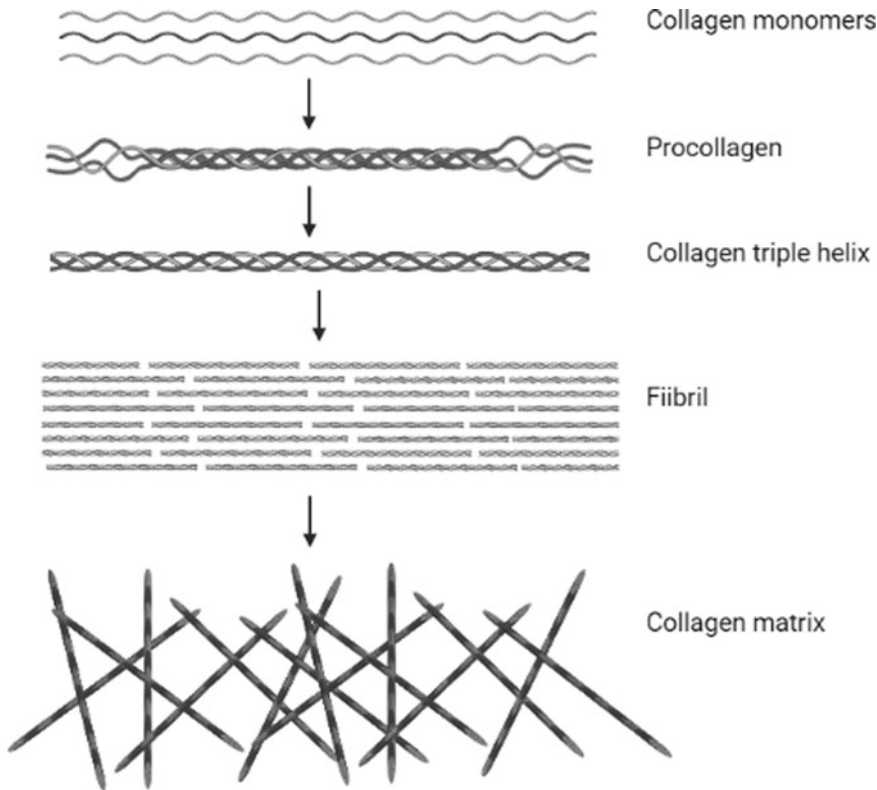


Fig. 4 Collagen structures and matrix formation (created with [BioRender.com](https://www.biorender.com/))

Several crosslinking methods are used to improve mechanical properties. Incorporating other polymers and biopolymers such as chitosan, keratin, silk fibroin, and even inorganic particles such as silver nanoparticles can create new polymeric materials.

As collagen shows film and sponge formation, this protein can be used to prepare biodegradable materials. New collagen sources have been investigated to avoid animal protein use. Modern meadows (<https://www.modernmeadow.com/>, accessed on November 3rd, 2021) developed a biosynthetic process using DNA editing tools to produce recombinant collagen in engineering yeast cells able to perform the hydrolyzation in the synthesized protein [56]. This new leather made from biosynthetic collagen is called Zoa.

Biofabricated leather is produced from collagen or a protein related to collagen, but not from animal skins like conventional leather. The collagen for the biofabrication of leather can be obtained from slaughterhouse waste or recombinantly produced *in vitro* by animal cells in a controlled culture or yet chemically synthesized. Briefly, to make biofabricated leather, the collagen needs to be isolated or purified in a solution to produce collagen fibrils by fibrillation. The next step is the crosslink formation of fibrils using a crosslinker agent as glutaraldehyde. After that,

the obtained film is dehydrated and lubricated, not necessary in this order, to acquire the leather characteristics [57]. The internal collagen structure of traditional leather and biofabricated leather is different. While the collagen arrangement in traditional leather is heterogeneous, the internal structure of a biofabricated leather is uniform, formed for disaggregated collagen fibrils randomly oriented throughout its volume. This leather can be used as a substitute for natural leather in any way, and its feel and appearance are similar to natural leather.

Biofabricated leather has some advantages [57, 58]:

- Biofabricated leather contains collagen primarily, and does not contain potentially allergenic proteins or other components found in traditional leather.
- Biofabricated leather has strength in all directions due to its uniform internal structure.
- Biofabricated leather presents flexibility comparable to natural leather.
- Biofabricated leather can have a soft grain texture on both sides.
- Biofabricated leather can display uniform thickness and consistency, uniform distribution of lubricants, crosslinkers, and dyes.
- Biofabricated leather does not tend to split parallelly to the sheet plane as traditional leather.
- During production processes, thickness, flexibility, consistency, smoothness, texture, or other functionalities can be controlled.
- The production process of biofabricated leather requires two weeks, so it is faster and cost-effective than traditional leather production if the animal growth time is considered.

3.2.2 Leather from Silk Protein

Proteins studied for alternative leather production have correlated characteristics such as self-assembly, multifunctionality, hierarchy, self-healing, and hydration. These characteristics are present in biological proteic structures silk and feathers and confer to the material tensile strength, hardness, flexibility, and durability, which can be exploited in new leather materials.

Silk is a material widely used for textile purposes for more than 4000 years and in medical sutures for centuries. Even though silk protein is known for so long, it can be applied to new materials. Leather-like material made from silk cocoons produced by *Bombyx mori* silkworms had been investigated [59]. The major proteins that compound silk are fibroin and sericin. Sericin is a protein found around fibroin acting as a glue that holds the fibroin fibers together. A thermo-chemical treatment can easily remove it.

Fibroin can be extracted from silk cocoons with a water-based process to produce a colloidal solution that can be used to obtain fibers, yarns, films, membranes, scaffolds, or sponges [59]. This solution assembles the protein solution present in the glands of insects such as spiders and silkworms and is used to produce fibers, films, and sponges by aggregation mechanism. Due to its biocompatibility, silk fibroin has been investigated as a biomaterial with medical applications [60].

A few are the works that explore fibroin to produce a material similar to leather. Among these works is the study of [59]. They use fibroin aqueous solution blended with glycerol and sodium alginate as a bioink to 3D using computer-controlled physical shearing of regenerated fibers through pressured-based extrusion printing. The methodology allowed the construction of layers with desired internal structures. To produce the leather-like material, they extruded the silk blend on a chitosan base layer. The thin chitosan base layer provided flexibility to the material, while the thick fibroin layer conferred adjustable tensile strength and stiffness. The obtained materials were robust, smooth, durable, flexible, and biodegradable.

3.2.3 Leather from Keratin Source

Keratin is an insoluble protein characterized by the high content of cysteine forming disulfide bonds. This protein compounds the epithelial tissues and its annexes as bird beak, hair, nails, horn, hoof, reptile scales, and feathers. After cellulose and chitin, keratin protein is the third most abundant polymer in the world [61]. Cao et al. [62] used chicken feathers, a structure consisting of 90% keratin, to develop a sustainable leather-like composite with applications in apparel and footwear products. Although the study did not analyze the properties of the composite, it opens the possibility of using feathers, an abundant waste of the poultry industry, as a component of alternative leathers.

Collagen, fibroin, and keratin leather-like materials have their production in aqueous systems processed with mild chemicals, employing conditions that minimize water and energy consumption and the amount and toxicity of waste. The perspective is that these new materials reach properties remarkably similar to natural leather with competitive cost.

4 Biopolymer as Tanning Agent

Biomass-derived polyaldehyde (BPA) is a biopolymer that has been investigated as a tanning agent. Chrome tanning is yet the most used tanning process in leather production due to the excellent properties of the finished leather by this procedure [63]. However, more than 60% of chrome is released in the tanneries' wastewater through subsequent leather processing steps such as neutralizing, washing, retanning, and dyeing. Chrome is also found in shavings and trimming solid wastes from leather that has undergone chrome tanning [64], causing widespread Cr pollution. In the present scenario, attention should be directed to chemicals used in the tanneries, looking for eco-friendly chemical options. Inorganic and organic tanning agents have been tested to substitute Cr in leather production so that the wastewater and solid wastes generated during the leather life cycle do not contain this harmful metal [64]. Wastewater issues have been widely addressed. However, little attention has been given to solid waste generated during leather manufacturing or leather itself

after use [65]. Waste leather produced by inorganic tanning usually takes more than 100 years for biodegradation, accumulating in the environment [66].

Petrochemicals and non-renewable compounds are traditionally used as organic tanning agents, but they are not, in turn, sustainable. Furthermore, the use of these organic tanning agents is usually accompanied by formaldehyde, another harmful chemical [64]. Consequently, new methodologies need to be developed to turn the tanning process more green and safe, making leather products sustainable and biodegradable after their lifetime.

Polyaldehyde (PA) has been extensively studied for tanning, especially dialdehyde carboxymethylcellulose and dialdehyde sodium alginate. These polymers are biocompatible, non-toxic, and biodegradable, features that meet the needs of eco-friendly chemicals for leather production [64]. Both dialdehydes have been obtained from different polysaccharide biomass sources such as carboxymethylcellulose, sodium alginate, starch, sugarcane bagasse, tara gum, and cyclodextrin [65, 67, 68, 69]. Cellulose and hemicellulose present in biomass can be hydrolyzed and oxidized to produce biomass polydialdehyde. PA is helpful as a tanning agent due to its abundant aldehyde groups, which bind to amino groups of collagen through crosslinks [70].

However, Ding et al. [68] observed that the mechanical strengths and thermal stability of PA tanned resulted in leather with poor quality. The low efficiency of PA is probably due to an imbalance between the aldehyde and amino groups of the collagen fibers, which can be overcome by adding more amino groups to increase the presence of crosslinking. Thus, the free aldehyde groups can react with the supplementary amino groups raising the collagen reticulation in PA tanned leather. The additional amino group can be offered by chitosan, another biomass polysaccharide composed of D-glucosamine and N-acetyl-D-glucosamine linked by β -(1 \rightarrow 4)-bonds. Numerous amino groups allow chitosan to react with polyaldehyde compounds to form a Schiff base structure, constructing new biodegradable and biocompatible materials with bacteriostatic properties [71]. The use of chitosan in the leather industry is not a novelty. It has been used in antibacterial coat compositions and as an auxiliary molecule in the dyeing process [72, 73]. Ding et al. [64] used the modified low molecular chitosan with dialdehyde carboxymethylcellulose (DCMC) for tanning. The polymer mixture improved the mechanical strengths and thermal stability, a better result than the previous study. The modified low molecular chitosan was obtained by oxidation using H_2O_2 and presented potential as an additive tanning agent in chrome-free leather production. Biopolymers abundant in dialdehydes and amino groups offer an alternative approach to avoid the leather industry's Cr utilization.

5 Biopolymer as Retanning Agent

Tanning, retanning, and fatliquoring are the most frequent steps in the hides transformation that may use polymers [74]. Petrochemical-based chemicals such as aldehydes, resins, and tannins are among the polymer materials usually applied in the leather industry. These chemicals are cost-effective and offer high quality of the leather, which justify their extensive use. There is currently a growing environmental concern about the massive use of petrochemicals used in a large scale. Thus, there is an increasing demand for renewable and sustainable alternatives to substitute those chemicals [75]. Excellent substitutes are the biopolymers that meet the needs of eco-friendly polymeric materials to make the industrial process more sustainable and the products more biodegradable.

Biopolymers extracted from vegetable and animal biomass of industrial wastes have been used as raw materials [75]. These industrial biomass wastes are usually treated enzymatically or chemically to produce lower molecular weight molecules, which are used to construct modified biopolymers with polyols, such as glycerol, and a condensation agent [75].

A raw material that can be used is leather waste. Several studies have reported the application of untanned collagen scraps or trimmings in the cosmetic and fine chemical industry as a higher value polymeric component [76]. The use of these residues increases the value of the leather production chain, allocating collagen-rich residues to products with more added value instead of using it as fertilizer, as has been done [52]. Sole et al. [74] used collagen from post-tanning waste as the raw materials to produce a biopolymer suitable for retanning. They reported a method combining enzymatic and chemical treatment to convert tannery byproducts into raw material to produce high-value biopolymers.

Scraps from chrome-tanned leather were enzymatically hydrolyzed in low molecular weight water-soluble molecules used as building blocks to generate biopolymers for retanning. These hydrolyzed proteins derived from bovine leather scraps (Bio-A) reacted with a polyol, glycerol, and maleic anhydride to produce Bio-IA intermediate. The synthesis of the intermediate was carried out to improve the number of carbonyl groups presented on the polymer responsible for the affinity of biopolymer with the collagen matrix of leather and make this intermediate a good candidate also as filling and fatliquoring agents [77]. Afterward, Bio-IA was copolymerized with acrylic acid to produce the final biopolymer (Bio-Ac). Bio-Ac demonstrates good performance as a retanning agent in leather processing, similar to acrylic resin retanning. The new biopolymer represents a sustainable substitute to usual retanning agents from petrochemicals.

Untanned waste (fleshing) has also been studied as a retanning/filling agent. Fleshing was hydrolyzed with a mixture of enzymes (peptidases, cellulases, and amylases) to obtain a retaining agent. This filler had the advantage of eliminating the step of salt purification of the retanning process, is cost-effective, biocompatible, and does not require hazardous chemicals like chromium, phenol, and formaldehyde.

Additionally, it can be employed to produce a wide variety of leather assortments [78].

Soy-derived biopolymer was investigated as a retanning agent. Soy hydrolyzed is a complex substrate containing a mixture of sugars (~30%), proteins (~40%), fibers (~10%), fat (~10%), and ash (~10%). This complex hydrolyzate as reacted with polyols and a condensation agent to produce the biopolymer. The leathers retained with the biopolymer exhibited good performances compared to the standard treatment. Treatment with soy biopolymer provided the leather with a well-filled crust, with fine grain and pleasant touch. All leather showed good dyeability, brighter color, and deeper hue than standard crusts [75].

6 Biopolymer in the Finishing Process

Finishing is the last process in leather production, which gives aesthetic characteristics to final products. Finishing is divided into base, intermediate, and top-coat. Base-coat uses solvents to modify the surface property of the crust and allows the fixation of finishing chemicals. Intermediate-coat enhances the physical properties through the use of binders for filling agents. Binders and fillers affect the pigmentation and the texture. Top-coat uses polymer materials such as polyurethane and cellulosic compounds to protect the finished leather. There are many finishing processes in leather manufacturing, and some of them may employ biopolymers, such as those mentioned below.

As a stabilizing of liposome-containing vegetable oil, pectin has been studied as a component of the fatliquor agent. Fatliquor is the liquors absorbed by the leather during fatliquoring. This process occurs after tanning and before drying, consisting to introduce oil into the skin. The principal purpose of fatliquoring is to manipulate the degree of fiber cohesion to ensure the structural integrity of the leather and avoid the fibril separation. However, excessive cohesion should be prevented once it can harden the leather, causing it to lose its value. Usually, the percentual of oil in the leather is about 3–10%. The leather features such as breaking stiffness, elasticity, handling, draping, durability, flexibility, and water resistance influence the fatliquoring process.

The oil needs to be emulsified in water or diluted in solvents to allow penetration and uniformity of fiber coverage in the leather. Usually, the oil is chemically modified by sulfation or sulfitation to become miscible in water. An example of synthetic fatliquor is sulphochlorinated hydrocarbons with 10–20 carbons in the chain [79].

Emulsification of the oils and water uses emulsifiers which are hazardous. The emulsifiers go to the effluent once the conventional fatliquoring leaves 10–15% of unbonded matter in the effluent containing also chlorinated paraffin oils and metallic soaps, alkyl phenyl ethoxylates, and non-volatile hydrocarbons [79]. So, this is not an eco-friendly process.

Bhargavi et al. [79] encapsulated vegetable oil in liposomes stabilized with pectin, a biopolymer used as a lubrication agent to create environmentally benign fatliquor. Pectin homogalacturonan backbone has ester methyl groups and hydroxyl groups

that make hydrophobic and hydrophilic, respectively, stabilizing the liposome lipid bilayers and promoting oil encapsulation in the hydrophobic region of the lipid bilayer. The stability conferred by pectin allows the fatliquor use at the drum conditions and good penetration of the active molecule. This work demonstrated that using an alternative fatliquor agent based on renewable materials eliminates the disadvantages of the traditional fatliquoring process [79].

Chitosan (CS) is a biopolymer obtained from chitin, an N-acetyl-glucosamine polymer. Shrimp and crab shells are the most usual source of commercial chitin. The chitosan is obtained from chitin through a reaction of de-acetylation with NaOH (40–50%) to form a glucosamine polymer. Chitosan and chitin have many functional properties, such as antimicrobial activity, high tensile strength, biodegradability, and non-toxicity, having many applications. Chitosan has attracted attention due to its antimicrobial activity against various fungi and bacteria [80]. Coatings containing chitosan have been developed to coat leather surfaces to prevent bacterial and fungal attacks [81, 82].

The priority in footwear industries is to produce comfortable, highly qualified, and health-safe footwear. To improve the hygiene and health safety of shoes, antimicrobial agent to prevent microorganisms' growth is desired by consumers [82]. Coating agents with antimicrobial properties are recommended once the collagen network of leather is an excellent harbor for microorganisms, which multiply in humid, warm, aerated, and with nutrient supply conditions. The leather colonization by microorganisms causes material deterioration, an unpleasant smell, and risks of infections [81].

Numerous natural and synthetic antimicrobial substances have been applied in leather to inhibit bacterial and fungal growth. Unfortunately, several approaches used to confer antimicrobial properties to leather use toxic compounds. Therefore, there is a necessity to develop safe and effective antimicrobial substances for leather coatings.

Antimicrobial coatings should be inexpensive, non-toxic, and active against bacteria and fungi. Silver nanoparticles have been used in coating materials due to their antimicrobial activity, non-toxicity, and eco-friendly characteristics. However, the process of their preparation is expensive [51].

Chitosan is a cheap material and has been currently proposed as an antimicrobial agent applicable in leather coating formulations. The CS with a broad intrinsic spectrum of antimicrobial activity and film-forming capacity was investigated in leather for footwear components [83]. The antimicrobial mechanism of CS coatings is similar to that of Ag nanoparticles. CS kills the microbial cell by promoting cell membrane damage. However, the activity decreases with time due to the presence of cell debris from dead microorganisms on the surface that reduces the antimicrobial efficiency [81].

Modifications or additions to chitosan have been proposed to improve the stability and activity. For instance, PEGylated chitosan copolymer (PEG-g-CS) was designed to produce a coating with high antimicrobial activity and antifouling properties conferred by PEG [81]. PEGylated CS prevented the adhesion of microorganisms

and showed higher antimicrobial properties than CS coating, indicating an antimicrobial synergetic effect of CS and PEG and an industrial potential as an antimicrobial coating for leather products [81].

To incorporate CS in coated leather, Mahmud et al. [82] performed a different strategy. In their study, chitosan with PVAc (polyvinyl acetate) coating was applied on crust leather surfaces. Polymeric PVAc is a binder agent with an easier and broader application, elasticity, resistance to aging, low cost, availability, resistance to microbial attack, and non-toxicity. The addition of PVAc enhanced the antimicrobial performance. Thus, PVAc-CS was investigated as a low-cost and eco-friendly alternative to inhibit microbial proliferation on leather products [82]. Even chitosan and chitosan derivatives are used in some chrome-tanned leather dyeing processes [83]; their use as a natural biocide is innovative, eco-friendly, and cost-effective.

Cellulosic compounds such as nitrocellulose, methylcellulose, carboxymethyl cellulose, and ethyl cellulose also find applications in the finishing process. Besides the top-coat agent, cellulose has been investigated in the intermediate-coat. Tamilselvi et al. [84] used cellulose extract from agricultural waste in the finishing process. Finishing formulations with and without cellulose were used to treat white crust leather, and the results showed that cellulose enhanced the leather properties like grain smoothness, proving that renewable cellulose sources can be applied in several finishing processes. Cellulose can also be used to improve the quality of leather with grain damages in leather.

7 Summary and Conclusions

Leather production is a growing global industry that severely impacts the environment with deforestation for breeding animals, massive consumption of water, and production of toxic wastes. Promising alternatives that highly reduced ecological footprints involve the substitution of leather by biopolymer composites or the use of biopolymer in several steps of leather processing. Cellulose leather, for instance, is not tanning through the chromium tanning process, and protein-based leather could eliminate chrome use by choosing bio-based tanning methods. Biopolymer in tanning, retanning, and finishing steps reduces the toxic waste from the most environmentally impactful phases of leather production. If the leather-like materials and processes described here can be cheap enough, it might offer the leather industry sustainable alternatives to conventional leather. Authentic eco-friendly leather is in greater and greater demand.

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Biopolymers in Automotive Industry



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Abstract Bio-based polymers are engineered for automotive applications due to their multifunctional characteristic properties, such as biocompatibility, biodegradability, and lower disposal as well as mechanical properties in some cases. Automotive Industry can shift to use renewable materials that exhibit equal or outstanding performance compared to the other conventional counterparts. Good life span and lightweight polymeric automotive parts as a way to reduce fuel consumption and therefore limit the outflow of ozone-depleting substances will continue to prompt comprehensive research into the applicability and employment of polymers and their obtained composites in the automotive industry. In this chapter, Biocomposite's Characteristic Properties containing biomaterials as Polymeric Matrix, i.e., Natural rubber, polylactic acid or Filler, Glass, Cellulose, Wood, Flax,..., in plastic and elastic parts, tires, and foams have been reviewed. Using biopolymers improves Tensile Strength and tear strength, Young's Modulus, higher Stiffness, lightweight, reduction in fuel consumption, lower Mooney viscosity, and better rolling resistance compared to conventional polymers.

Keywords Biopolymer · Natural · Automotive · Bio-based composites · Plastic · Elastomer

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1 Introduction

There are many waste products in the automobiles' whole life cycle, including vehicle production, usage, disposal, and recycling. It is reported that the industry generates almost 9 million tons of waste annually during automobile parts disposal [1]. This number would be much higher by the ascending trend of motor vehicle production, represented in Fig. 1 [2], so recycling would be vital to save the environment. By using biodegradable materials in car production, it would be easier to recycle vehicle parts after the scrap.

On the other hand, during usage, there is an enormous volume of carbon dioxide emissions. By decreasing the vehicle's weight by 100 kg, the fuel consumption would reduce to almost 0.35 L per kilometer [3]. The lower the fuel consumption, the lower the carbon dioxide emission. One of the approaches to reduce the vehicle weight is to use polymers in its parts.

In the automotive industry, polymers are playing essential roles. Their functionality, resistance to corrosion, longer lifetime, the flexibility of integrating parts, being safe, economical, and low weight which lead to decreasing fuel consumption are the main reasons for using polymeric parts. Polymers are used in bumpers, seating, fuel system, dashboard, body, interior/exterior trim, panels, under-bonnet components, electrical components, lighting, upholstery, liquid reservoirs, car tires, etc.

The average weight of polymeric materials used in vehicles increased from 50 kg/car in 1970 to 157 kg/car in 2019, and it still has its growing trend until now [4].

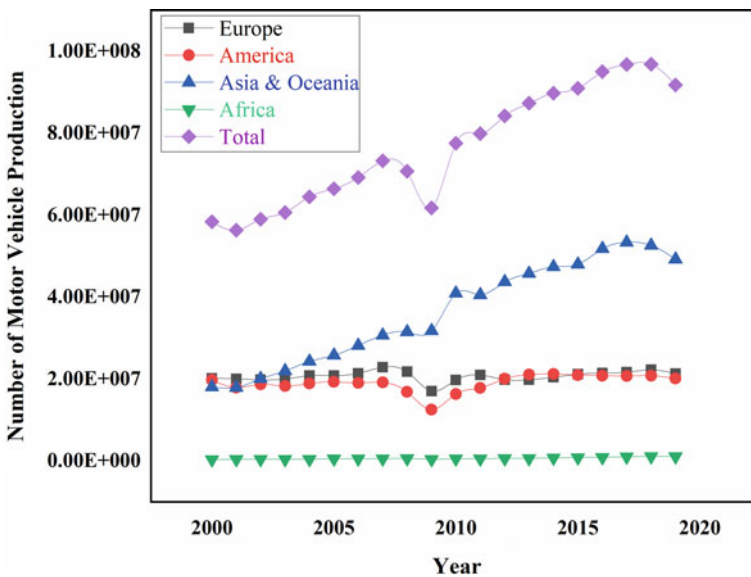


Fig. 1 The numerical trend of the production of the motor vehicle by region per year

Automotive production chains have a significant impact on the environment, production, usage, and, of course, disposal. Due to the growing trend of producing motor vehicles, as shown in Fig. 1, it is vital to use biopolymers or use bio-additives in traditional polymers. In this paper, we tried to categorize biopolymers into plastics, elastomers, and foams. In each category, we introduce biopolymers, or biodegradable additives in plastics, elastomers, and foams, and discuss the effect of using biomaterials in final product properties.

2 Plastics

Lightweight vehicles are one of the most significant markets for polymeric composites and plastics, which have been growing within the last five decades. Recently announced statistics, Fig. 2, have revealed that the North American light vehicle currently contains about 355 pounds of polymeric composites, which would be about 8.9% of the total weight. This was recently announced that plastics make up nearly half of the volume of the new lightweight vehicles but not as much as 10% of the vehicle's weight. This will ensure lower fuel consumption and so fewer greenhouse emissions [5].

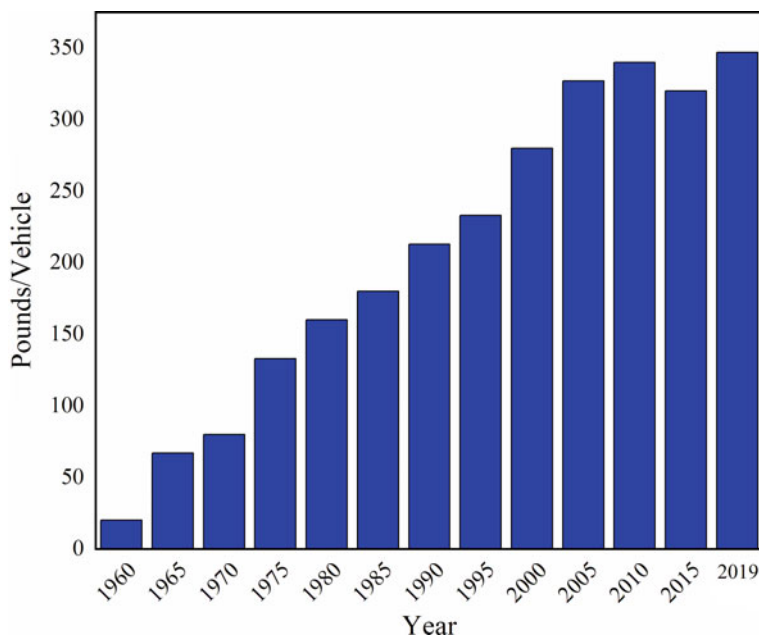


Fig. 2 Long-term trends in NAFTA (North American free trade agreement) light vehicle employment of polymeric composites (pounds/vehicle)

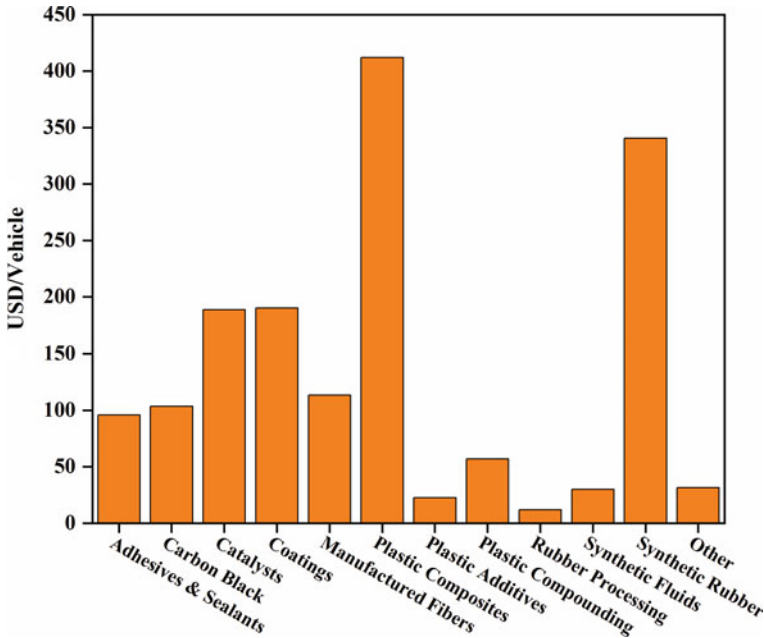


Fig. 3 The average use of polymeric composites in North American light vehicles (NAFTA) in 2019 (pounds/vehicle)

Over 15 polymeric resins are employed in the automotive industry. The most common types are polypropylene (PP), polyvinyl chloride (PVC), polyurethanes (PU), nylon, polyethylene (PE), acrylonitrile–butadiene–styrene (ABS), and polycarbonate resins. The details on pound/vehicle use are provided in Fig. 3 [5].

Many bio-based composites have been introduced to the automotive industry for obtaining low-weight vehicles. These bio-based composites can be obtained with the aid of biopolymers including Polylactic Acid (PLA) [6] by employing bio-based reinforcements into the conventional polymeric resins [7–11] or employing both bio-based resin and bio-based reinforcement simultaneously [12–16]. The following are some of the recent publications in this area.

Wei and coworkers [6] introduced a novel bio-based aromatic polyamide composite and its application in automotive biofuel supply systems. In this study, glass fiber-reinforced highly bio-based semi-aromatic polyamides (polyphthalamide, PPA) were fabricated, and the PPA matrix assessed both bio-based diesel and petroleum absorption. It was revealed that PPA had better barrier properties, confirmed by its low and slow fuel uptake.

The copolymer was produced with the aid of an 11-aminoundecanoic acid monomer. The glass fibers were first coated by a silane coupling agent and then added to the polymer matrix. About 0.5wt.% carbon black was added as UV stabilizer and coloring agent. The as-received GF30-PPA (with 30 wt.% of glass fibers) and GF23-PA12 (the glass fiber content was 23 wt.%) dumbbell specimens were aged

in petroleum diesel with the aid of autoclaves. The samples were stored at about 125 °C, and the replacement of the fuels was carried out every two days to be the same as the refueling process. After 280, 560, and 700 h of aging, samples were stored in plastic bags at 4 °C until the test time.

The tensile-fractured surface was studied by SEM analysis. The fiber pull-out was obvious for both aged and unaged specimens suggesting that the significant fracture mechanism is polymer failure. A layer of polymer with 1 μm thickness was observed in the unaged sample, indicating the fibers' good adhesion into the PPA matrix. When exposed to the fuels at high temperatures, acceptable mechanical properties confirmed that the fuel could only affect the polymer matrix but not the polymer–fiber interactions.

In another research, Sadashiva and coworkers [7] synthesized a new hybrid biocomposite consisting of drumstick and glass fibers within a polyester matrix. An easy hand layup technique was employed for composite fabrication, and the fibers' orientation was studied. For this purpose, woven mats were cut and placed at the mold's surface; already prepared polyester resin and its curing agent in liquid form were added to the mold and spread carefully. The drumstick fibers were then placed on the polymer surface as the second layer and the roller was gently moved to eliminate the excess resin and any trapped air. Two specimens with different fiber orientations, longitudinal and transverse, were prepared for tensile tests. This was observed that the orientation of fiber composites can affect the properties. The authors concluded that the composite specimens fabricated by the longitudinal orientation of fibers have better properties.

Silva and Frollini [8] have recently investigated the employment of fibers obtained from sugarcane bagasse (SBU). The thermoset phenolic resin was employed as the polymeric matrix. The phenolic resin was prepared by the following weight ratios of 1.38: 1.0: 0.06 of phenol: formaldehyde: KOH. The sugarcane bunt bagasse (SBB) fibers were compared to SBU fibers. Although there are no significant differences in the structural compositions of both types of fibers, the inverse gas chromatography (IGC) revealed that the SBU surface is full of polar groups, which enhances the intermolecular interactions and improves the interaction to the matrix. Three different sizes of the fibers, 1, 3, and 5 cm, were compared. The impact strength was improved for all tested lengths; however, the longest fibers, 5 cm, showed a slightly lower improvement than the others. On the other hand, this fiber showed lower water adsorption property, making that a good candidate to be employed in situations in which water resistance is a critical factor.

In another study, Al-Oqila and coworkers [9] studied the applicability of using the date palm fibers (DPF) as bio-based reinforcement in the natural fiber-reinforced polymeric composites (NFC) and their application in the automotive industry. The authors claim that by this approach, a novel reinforced biocomposite is fabricated, and at the same time, the date palm waste issue is addressed. Several comparisons, including aspect ratio (L/D), thermal conductivity, and world production content, were carried out between the DPF and other common fibers. DPF represented better properties in many studies. The date palm fibers are considered to be very cheap (about 0.02\$/Kg). DPF demonstrated a specific Young modulus to price ratio of

about 80 GPa/(g/cm³) compared to Coir, Hemp, and Sisal. The authors suggest that employing DPF in the automotive industry will improve this industry as well as address the environmental waste issue.

In a recent study, Yusof and coworkers [10] introduced a conceptual design of an automotive crash box (ACB) reinforced with oil palm polymer composite. In this research, the design which got the highest score was selected as the best design. This outer part had a honeycomb structure, and the inner part had a spider web structure. A fiber foam structure supported the design to improve the energy absorption ability of the final composite. The bending collapse is known to be the primary cause of failure for ACB during the collision. The impact properties of natural fiber-reinforced ACB suggested that this new design can be substituted by conventionally used materials such as aluminum alloys and steel alloys in automotive industries.

The bio-based plant fibers, including alfa, flax, and cellulose fibers, are widely replaced by synthetic glass fibers in automotive industrial applications. These natural fibers are well known for their low density, high mechanical properties, and being environmentally friendly. In this regard, Pantaloni and coworkers [12] have recently published an article in which a completely green bio-based composite was produced consisting of three biodegradable polymers, polybutylene succinate (PBS), polyhydroxyalkanoate (PHA), and polylactic acid (PLA), and nonwoven flax fibers. The obtained composite had the same performance as the one currently used in industry, polypropylene (PP)-reinforced nonwoven flax.

For polymer film manufacturing, the granules were dried in the oven at 60 °C for 12 h, followed by extruding and calendaring to prepare the polymer films. The composite was made by film stacking, considering that the temperature plays a critical role in well-impregnating. The temperature was adjusted to 200 °C, and the time for exposure was set to be 8 min. The authors suggest that flax fibers will keep their mechanical properties by setting time and temperature in this range.

The authors suggest that all flax-reinforced biodegradable polymeric composites in this research had better mechanical stiffness and strength than PP reinforced with flax. Moreover, the flax/PLA lost about 37% of its strength only after the sixth day of being buried in garden compost. About 50% of strength loss was observed for all the biocomposites after 190 days, which is significantly higher than the flax/PP. Possessing high mechanical properties even after exposure to harsh conditions and biodegradability simultaneously have made these biocomposites a promising candidate for automotive, industrial use.

Oliver-Ortega and coworkers [13] researched the design and development of automotive parts using wood fiber-reinforced bio-based polyamide 11 composites. They carried out some novel investigations on the reinforced composite's mechanical behavior when employed as a car door handle. They suggest that using 40–60 w/w natural reinforcement can be effective in this composite to replace synthetic ones such as glass fiber reinforcement materials in the automotive industry.

The fabricated composite consisted of a stone groundwood cellulose-based reinforcement (SGW) coupled with a polyamide 11 (PA11) bio-based matrix. The results revealed that the composite possesses high mechanical properties. Changing the fiber content from 10 w/w to 50 w/w leads the tensile and flexural properties to enhance

linearly, representing that the fiber is well dispersed in the mixture and an effective interface exists leading to a thriving load transfer. The optimum SGW content was reported to be 50 w/w in which the maximum flexural and tensile strengths of PA11 composites were measured to be 63.9 and 92.6 MPa, respectively.

A case study was carried out to design an interior door handle of a car. Computational analysis was used for assessing the part in the standard and limited condition. The analysis showed that by employing at least 40% w/w of the SGW, the obtained composite could be replaced by the original component. The maximum deformations and the safety factors of the obtained composite would be the same as the traditional one.

In a research carried out by Birch and coworkers [14], a cost-effective and sustainable approach was reported to develop high strength modulus and lightweight material for automotive applications. In this research, composites based on bio-based polyamide blends and cellulose fibers with different weight percentages were prepared. The mixture was extruded at 230 °C. Twice extruding was done to ensure the even distribution of cellulose in the polyamide. The mixture was then injection molded at a maximum temperature of 246 °C. Before extrusion and injection molding, materials were all dried overnight at 70 °C. They suggested that the tensile and flexural modulus increased with increasing filler content. The tensile strength stayed approximately the same level with up to 20 wt.% cellulose content, but a reduction was observed at 30% due to the filler loading interference with the matrix's stress-transfer ability. The flexural strength was the highest at 20% cellulose content. The notched Izod impact strength results showed a decrease with an increase of fiber content. However, there was no significant reduction until 30% cellulose content. Increasing the interfacial regions and, therefore, crack propagation, fibers' addition will reduce the impact strength. The thermal gravimetric analysis (TGA) demonstrated that enhancing the cellulose fiber content slightly reduces the temperature at which 10 wt.% is lost. The Polyamide blend performed well in TGA analysis by representing an intermediate property between the two different polyamides.

The interfacial adhesion is known as a critical issue, the bio-based fibers and bio-based thermoplastics interfacial adhesion is a drawback that restricts the large-scale production and application of biocomposite materials. In this regard, the fiber treatment effect was investigated on the properties of the final biocomposite by Werchefani and coworkers [15]. Polylactic acid (PLA) and Alfa short fibers were chosen as matrix and reinforcement, respectively. The authors suggest that these natural fiber-reinforced composites can be employed in industries such as automotive applications.

Three different types of Alfa fiber treatment were carried out with the aid of NaOH, xylanase, and pectinase. The untreated fibers were employed as the blank sample. The chemical compositions were assessed by biochemical analysis. The SEM analysis revealed that the chemical and enzymatic treatments had changed both the composition and the topography of the fibers. For untreated fibers, the fibers' bunches were detected, suggesting waxy materials holding the fibers together. After chemical treatment, the surface of fibers indicated that some of the constituents, including hemicellulose and lignin, are removed, and the fiber bundles have been opened.

The samples treated with xylanase and pectinase showed the same morphological properties. The splitting of the fibers could obviously be detected, and the fibrils had come into contact. Also, the more isolated and finer fibrils could be detected in pectinase-treated fibers.

Tensile analysis revealed that fiber modification plays a critical role in the obtained composite mechanical properties. It was observed that the enzymatic modification provides a dramatic increase in the tensile modulus and tensile strength. The Alfa fibers treated with pectinase revealed the highest tensile properties when employed as the reinforcement of the PLA matrix. This can be attributed to the pectinase treatment's morphological changes, which separates fibers into individual fibrils, as confirmed by SEM analysis.

In another research, recently published by Platnieks and coworkers [16], five compositions were prepared by nanofibrillated cellulose (NC) and microcrystalline cellulose (MC) as fillers and bio-based polybutylene succinate as the polymeric matrix. The melt blending approach performed the composite fabrication. The synergistic effect of the application of nano and micro cellulose into the polymeric matrix was investigated.

Differential scanning calorimetry revealed that nucleation and crystallization occur in both fillers. However, the MC filler can improve the crystallinity degree more than the NC filler. It is well known that the cellulose filler structure affects the crystallization process, and the agglomeration of the fillers can decrease crystallinity. Two different crystallinity values were observed for 40% NC and 40% MC composites confirming the effect of the filler structure on the degree of crystallinity. By increasing the composite's MC content, the degree of crystallization showed an increase, and the splitting in the melting peak represents the trans crystallization. This was concluded that NC forms larger agglomerations due to its higher surface area and stronger hydrogen bonding. This results in an uneven filler distribution. The MC was chosen as a more suitable candidate for industrial applications, including automotive plastic parts.

Many characteristic properties were obtained by using bio-based plastic composites in the automotive industry. The significant ones are summarized in Table 1.

3 Elastomers

Elastomers are widely used in the automotive industry due to their unique properties. They are mainly used in the interior designing of vehicles and also tires. Thermoplastic urethane (TPU) and natural rubber (NR) are the most majorly utilized elastomers in the automotive industry. Using thermoplastic polyurethane elastomers can result in better ultraviolet resistance, reduced thickness, and better mechanical properties. Additionally, the rising demand for lightweight vehicles has resulted in the remarkable growth of the elastomers market in the automotive industry.

As the elastomers do not have enough wear resistance and acceptable mechanical properties, they need to be reinforced with some fillers. On the other hand, relaxation

Table 1 Characteristic properties obtained by using bio-based plastic composites in the automotive industry

Polymeric matrix	Filler	Bio-based component	Biocomposites characteristic properties		
			Tensile strength (MPa)	Young's modulus (GPa)	References
Polyphthalamide	Glass fiber	Matrix	~140 (20 Wt.%)	~6 (20 Wt.%)	[6]
Polyamide	Cellulose fibers	Fibers	~50 (20 wt.%)	~3.6 (20 wt.%)	[14]
Phenolic thermoset	Cellulose fiber	Fibers	–	~4 (30 Wt.%)	[8]
Polyamide	Wood fiber	Fibers	–	~5 (50 Wt.%)	[13]
Polylactic acid	Flax fiber	Fibers/matrix	~100 (30 Wt.%)	~13 (30 Wt.%)	[12]
Polylactic acid	Alfa fibers	Fibers/matrix	~66 (20 Wt.%)	~3 (20 Wt.%)	[15]
Polybutylene succinate	Cellulose fiber	Fibers/matrix	~22 (40 Wt.%)	~6 (40 Wt.%)	[16]

of the elastomeric polymer chain and viscous dissipation in the elastomeric system leads to a large amount of fuel consumption. Considering the increasing trend of automobile production, this will be a remarkable issue. The more the fuel consumption, the more CO₂ emission and of course the more air pollution. As a result, using environmentally friendly components would be a solution. Some of the popular automobile producers started to use bio-based additives to the elastomers used in door panels and course tires [17].

As discussed above, the degradability of thermoplastic elastomers used in the automotive industry has attracted a lot of attention for its environmental issues. In this subject, many researchers are trying to introduce a new generation of thermoplastic vulcanisates (TPVs) with environmentally friendly specifications compared to traditional TPVs. Therefore, the researchers started to use bio-based TPVs, for example: TPVs based on poly(lactic acid)/Natural rubber, TPVs based on poly(lactic acid)/ethylene–vinyl acetate, and TPVs based on poly(butanediol–lactate–sebacate–itaconate) elastomer (PLBSI)/PLA [18]. In this regard, Audi A2 used hybrid mats based on sisal/flax-filled PU as vehicle door trim panels in 2000 [19].

The effect of using cellulose nanocrystals in improving polyurethane matrix has been investigated by Aranguren et al. [20]. It was shown that by using 0.5, 1, and 5 wt% of nanocrystal, the storage modulus was found to show an increasing trend.

The first commercial application of natural fibers in polyurethane was in S-Class Mercedes-Benz in 1999 in its door panel. In this automobile, for its 2-mm thick door panel, 65% flax/hemp/sisal fillers were added to 35% semi-rigid polyurethane

[21]. At a constant weight, the panel shows higher mechanical strength and stiffness. Some automotive producers, such as Audi, Mercedes, and BMW, have used this unique structure (lightweight honeycomb structure inside, with fiber-reinforced polyurethane shell) which has been also used in door panel and other trim parts, sun shades, spare tire covers, and load floors [17, 22].

The first time when Toyota started to use biodegradable polymers involves using Kenaf fibers in PLA matrix from sugarcane and sweet potatoes in spare tires of its RAUM 2003 [23]. Then for producing door trims in Mazda, a composite containing polypropylene reinforced with kenaf fiber was used. In 2008, in Rav-4, Toyota also used seat foams based on soybean. At the same time, for Lexus CT200h, biodegradable polypropylene/poly(lactic acid) was used in manufacturing the side trims, floor finishing plate, toolbox area, door scuff plates, and package trays [24].

Anuar et al. [25] investigated the mechanical properties of thermoplastic natural rubber and polypropylene/ethylene-propylene-diene monomer (PP/EPDM) filled with Kenaf fiber. They believed the development of PP/EPDM reinforced with Kenaf fiber has the ability to be used in automobile parts.

4 Green Tires

The green tire technology was introduced in 1992 by Michelin company using silica plus a bi-functional silane, bis-(triethoxysilylpropyl)tetrasulfide in tire treads instead of carbon black in Europe due to consumer appreciation for better handling, energy cost, and environmental issues. The demand for green tires now has an increasing trend in the world [26].

In the Goodyear company, it was shown that using silica along with carbon black in the tire formulation would result in a 50% reduction in rolling noise, about 10% in wet traction, and 5% reduction in the consumption of fuel and of course air pollution. [27].

For this remarkable innovation, they were awarded at the Geneva Motor show [17]. In spite of the fact that polyisoprene derived from natural rubber has optimum properties, there is some problem using them and the tire producers should shift to replace it totally or partially. One is the shortage of resources in some areas and the next is the environmental issues. So, in tire manufacturing, it has been considered to utilize a type of isoprene which is bio-based.

Woody biomass, switchgrass, and molasses of sugarcane have been shown to be utilized as an acceptable alternative for natural rubber-derived polyisoprene. Mevalonic acid and also 1-deoxy-D-xylulose-5-phosphate pathways by using fermentable sugars as feedstock were utilized to generate the precursors for the synthetic bio-based polyisoprene [28].

In filled polymeric systems, many factors can affect the tire rolling resistance. These parameters include dispersion state, aggregate structure, macromolecular structure, and, of course, interfacial properties. The rolling resistance coefficients of tires and the amount of the elastomers loss modulus at 60 °C are laboratories and industrial benchmarks for automobile fuel consumption. For decreasing fuel

consumption, wear resistance, and also wet traction, the most important part to be considered is the tire tread, as this part is the main elastomeric part of the product.

An important safety parameter for a tire is wet traction. Because with a sufficient tire wet traction, dissipation of energy in the using of the braking system would be good enough. For an optimum wet traction, the loss tangent should be high at 0 °C. But at the same time, at 60 °C, the loss tangent should decrease. A good commercialized option for use in tire tread manufacturing to make green tires is anionic solution styrene–butadiene rubber which is reinforced with silica particles [29]. This material has the specifications described above.

Dominic et al. [30] have studied the effect of reinforcing natural rubber with Rice Husk-Derived Nano-cellulose (RHNC) instead of carbon black in tires. They showed that the scorch time and curing rate were improved when they used 5% RHNC and 25% carbon black instead of 30wt% carbon black. The tensile strength and tear resistance of both samples were shown to be almost the same. The technological properties and also swelling index show comparable results in both composites. The stress transfer was shown to be effective in both composites. The presented method in this research can be extensively applied in automotive tires, rubber reinforcement, and other green elastomeric materials.

One of the challenges of using silica in tire tread composition is its dispersion. In another research, Lolage et al. [31] have utilized highly dispersible bio-based silica (HDS) instead of carbon black in the composition of tire tread. They believed that the HDS which is obtained from rice husk ash would cause better dispersion, 15% decreased sample viscosity, higher tensile strength and elongation at break rather than normal silica, and better dispersion. Finally, they conclude that their method leads to an environmentally friendly process that produces a valuable product from the agricultural waste.

The annual value rate of the green tire market is predicted to be 20.63%, and the annual volume rate is predicted to be 22.57% during the forecast period. It has been predicted that the green tire market will be worth USD 152.40 billion by 2023. The key manufacturers of the green tire are Michelin, The Goodyear, Pirelli & C. S.p.A., Kumho Tire, Continental AG, Bridgestone Corporation, Hankook Tire, Cheng Shin Rubber Ind. Co. Lt., Zhongce Rubber Group Co., Ltd (ZC-Rubber), and Nokian Tyres plc [32].

Due to the growing demand for silica in green tires and low interfacial compatibility between silica and NR compared with carbon black and NR, renewable and non-toxic processing aids are required. Some researchers tried to solve this problem. Song [33] used multi-alcohol parts of hydrophilic and hydrophobic groups as a processing aid to increase compatibility between NR and silica. They showed using this processing aid would finally lead to enhanced dry and wet braking performance and durability at high speeds. In another research, Das et al. [34] used a new SBR grafted-(novel 3-Octanoylthio-1-propyltriethoxysilane) in nano silica/3-Octanoylthio-1-propyltriethoxysilane grafted on SBR composite. Their results showed that tensile strength, tear strength, and also rolling resistance of the composites were shown to be better using this grafting agent. In another

research, Hassan et al. [35] used soybean oil-derived silanized plasticization for compatibilizing SBR and silica particles.

According to the increasing use of silica-based green tires, some researchers focused on chemical functionalization and devulcanization of waste SBR [36], and also by pyrolysis of waste green tires [26]. Jiang et al. [37] have recently used Silica-graphene hybrid (HGKS), with different hybrid grafting ratios, in natural rubber to be used in the tire tread. They believe in this composition. There is an excellent interfacial interaction between polymer and matrix, which is the essential factor in determining the rubber composite performance used in green tires.

Saleem et al. [38] have fully described using natural fibers as a hybrid with carbon, glass, and basalt fibers in polymers used in the automotive industry.

Another strategy for solving economic issues of using elastomers in the automotive industry is using bio-compatible resources to make elastomeric materials. Some of them which have been commercialized are polyhydroxyalkanoates [39], polylactide [40], and poly(butylene succinate) [41]. Elastomers based on Soybean [42, 43], poly(diisooamyl itaconate-co-isoprene) rubber [44], and polyester elastomers have already been previously investigated. However, for tire applications, no bio-based elastomer has been formulated until now. But research is still being continued in this area.

Li et al. [45] have recently used trans-1, 4-poly (butadiene-co-isoprene) (TBIR) in tire tread formula. They showed a composite containing carbon black-filled TBIR/NR/ESBR showing a reduced rolling resistance and a significant fatigue and abrasion resistance. They introduced this composition as a good candidate for tire tread of automobiles. The effect of using bio-derived elastomeric composites has been summarized in Table 2.

5 Foams

One of the essential topics has become CO₂ emissions due to high fuel consumption in the automotive industry in recent decades. One of the promising solutions would be the production of lightweight vehicles in which metals replace polymers. Foams are widely used as acoustic materials in this regard. However, most commercial materials contain harmful chemical compounds or time-consuming fabrication processes [46]. Employing bio-based materials in foam formulations has introduced more comfortable and safer fabrication conditions. Moreover, biomass is sustainable and renewable compared to fossil resources, and this alteration would be noticeable and crucial for human life [47].

Mazzon and coworkers [46] introduced a novel highly reactive epoxy foams in 2015. This project aimed to investigate the efficacy of this new foam in reducing the vehicle weight and, therefore, fuel consumption. Exothermicity regulators were employed in foam making, due to their endothermic dehydration reaction. Different foams with various compositions were prepared and characterized. The authors claim

Table 2 Characteristic properties obtained by using bio-based elastomeric composites in the automotive industry

Polymeric matrix	Filler	Bio-based component	Biocomposite's characteristic properties	References
Polyurethane	Cellulose nanocrystal	Filler	Increasing Young's modulus from 50 to 110 MPa	[20]
Polyurethane	65% flax/hemp/sisal	Filler	Higher Stiffness, light weight	[17]
Natural rubber	Silica + carbon black	A part of filler	5% reduction in fuel consumption	[27]
Natural rubber	Bio-based highly dispersible silica	A part of filler	15% lower Mooney viscosity compared to conventional silica, better dispersion, better reinforcement factor (from 4.2 to 4.5), higher tensile strength(from 130 to 180 kg/cm ²), and elongation at break(from 293 to 426%)	[31]
3-Octanoylthio-1-propyltriethoxysilane grafted SBR	Silica	Filler	Higher tensile and tear strength, better rolling resistance	[34]
Biomass-derived isoprene	Carbon black	Matrix	Comparable with traditional Helping environmental issues	[28]
PLA derived from sugarcane and sweet potatoes	Kenaf fiber	Both matrix and filler	Increasing mechanical strength up to 70 MP and storage modulus up to 6 GPa	[23]

that highly effective foams can be easily obtained in a few minutes by the suggested components and approach.

Recently, in 2020, Mazzon and coworkers [47] published new bio-based epoxy foams by mixing two epoxidized plant oil-derivatives with a non-toxic foaming agent and anhydride hardener. Highly reactive epoxy foams were prepared in less than 3 min. The effect of thermal domains and the blowing agent's decomposition was studied on the final foam production. They revealed that the best characteristics could be obtained by choosing a blowing agent who starts acting when the crosslinking has almost finished. In other words, the trap of gas in the polymeric matrix can be carried out with no effect on the crosslinking degree.

Sound isolation is one of the critical issues in automotive parts, including dashboards and door panels. In this regard, many researchers focus on developing new bio-based foams for application in automotive industries. Rus and coworkers [48] have published a recent article related to this issue. In this paper, a novel biopolymer foam was fabricated by employing biofillers. Wood dust and tire rubber waste were used as fillers, and the cooking oil waste was converted to the monomer. The hybrid fillers percentage was set as 2.5%, 5.0%, 7.5%, and 10% weight to weight ratio with bio-monomer. The foam with 10.0% fillers revealed the highest sound absorption coefficient ($\alpha = 0.963$). This filler loading, 10.0%, resulted in the smallest pore sizes, but the pores were interconnected, leading the air molecules within the pores to vibrate. This vibration would reduce the original energy of the air molecules. This was concluded that the biocomposite fabricated from wastes could be effectively used in the automotive industries' acoustic application.

Polyurethane foams are highly considered in the automotive industry regarding their acoustic properties. In this regard, Ji and coworkers [49] have recently introduced a novel polyurethane foam based on tung oil (TOPUF) by employing miscanthus lutarioriparius (ML) to improve acoustic performance. A one-step synthesis procedure was used for composite fabrication. For this purpose, polyols and methylene diphenyl diisocyanate were used for polyurethane foam synthesis. Silicone and Deionized water were added as foam stabilizers and blowing agents, respectively. The filler, ML, was added to the polyurethane foam, including NaOH solution (5 wt.%) as a treatment solution for filler. All the reagents except methylene diphenyl diisocyanate were mixed for 20 s. followed by adding the ML and methylene diphenyl diisocyanate to the mixture and stirring for more 10 s. The foam was fabricated by molding for 60 min at 50 °C. The common behavior was observed in all samples, by adding various amounts of ML. This was suggested that the cavity size will be decreased by increasing the content of ML powder. The optimum acoustic properties were obtained at 0.3 wt% of ML. The transmission loss and the average sound absorption coefficient were measured to be 19.05 and 0.518 dB, respectively. The authors claimed that the suggested method and the fabricated foam can fabricate acoustic materials, specifically in the automotive industry.

The addition of Lignin as a non-toxic, inexpensive, and abundant component into the polyurethane (PU) foam was another strategy for developing reinforced biocomposites in automotive industries. In this research, Faruk and coworkers [50] carried out a green PU foam with the aid of soy polyol. The isocyanate content,

with potential health hazards, was reduced by introducing lignin to PU foam. It was reported that the foaming procedure was delayed due to the addition of fiber. The presence of fiber also hindered the expansion of the polymer matrix. The SEM analysis of the foam revealed that the addition of lignin had reduced cell size in PU foam. However, no meaningful change was detected in the cell shape and roundness.

Yu and coworkers [51] have introduced novel non-isocyanate polyurethanes by employing bio-based poly(cyclic carbonates) and amines. The effect of catalysts was investigated, and the properties of the final coating were studied in this research. Carbonated Soybean Oil (CSO) was synthesized with the aid of CO₂ and ESO. Tetrabutylammonium bromide (TBAB) was used as a catalyst. Once finished all solvents were removed with the aid of a rotary evaporator. The Carbonated Sucrose Soyate (CSS) was prepared by the same method with some modifications. It was suggested that the higher functionality of the CSS could effectively improve the coating properties.

6 Conclusion

The contribution of polymer composites has significantly grown up in the automotive industry, regarding their unique properties. Light vehicles have represented an essential market for plastics and polymer composites during the last five decades. Polymeric composites, including plastics, elastomers, and foams, are widely employed in lightweight automobiles and have paved the way for becoming a vital part of the automotive industry. In recent decades, green synthesis and bio-based materials have gotten worldwide attention, and the automotive industry is a pioneer in this field. Due to their improved environmental applications and recyclability, automobile manufacturers are eager to employ bio-based materials. It is approved that the recycling of bio-based fillers requires lower energy than commercial reinforcements such as glass fibers.

Using natural fibers for reinforcing polymers used in the automotive industry has some drawbacks despite having the benefits mentioned before. They are more flammable than traditional fillers. Their mechanical properties are not as high as traditional ones. They need lower processing temperature, and because of their nature, they are not compatible with hydrophobic matrices, so there are some mixing issues. Another challenge is the non-uniformity and non-reproducibility of the natural fibers due to their different ways of extraction. One way to overcome these drawbacks is to use hybrid composites. However, it is still a challenge to use biodegradable fibers.

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Biopolymers in Electronics



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Abstract Electronic devices fabricated using biopolymers are considered environment-friendly electronic devices that attract researchers' interests in addressing non-biodegradable polymers. Biopolymers are renewable, abundant, relatively cheap, biodegradable, and environment-friendly. Biopolymers also have the potential to be applied in electronic devices. This study reviews the practical application of both natural and synthetic-based biopolymers in electronics. The biopolymer is generally non-conductive, so it requires modification to increase its electrical conductivity, so it can be applicable in electronic devices.

Keywords Biopolymer · Conductivity · Electronic

1 Introduction

Research on developing alternative materials in the form of biopolymers as a substitute for plastics has grown rapidly. These developed biopolymers are predicted to reduce and replace dependence on non-renewable resources and minimize environmental pollution that may arise from the use of plastics in various fields such as in electronics. Flexible electronics from plastic materials have not been designed to be disposable, primarily because of the environmental issues related to their biodegradability. Electronic devices fabricated using biopolymer are considered environment-friendly electronic devices that have increasingly attracted researchers' interests in addressing non-biodegradable polymers. Biopolymers are renewable, abundant, relatively cheap, biodegradable, and environment-friendly [1]. Biopolymers have some electrical properties that have the potential to be applied in electronics devices such as batteries, capacitors, supercapacitors, active electrode materials, sensors, displays, transistors, memory, active anode as well as ions and electrical conductivity. These properties make them a suitable material for the fabrication of electronic devices

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[2]. This work discusses the application of both natural biopolymers such as cellulose, starch, and chitosan, as well as synthetic-based biopolymers such as polylactic acid-based, polyvinyl alcohol-based, polyhydroxyalkanoates-based, and poly(ϵ -caprolactone)-based biopolymers.

2 Natural Biopolymers in Electronics

2.1 Cellulose

Cellulose is a bio-renewable macromolecular polysaccharide that is abundant in nature. Cellulose has a high strength matrix and dense structure due to a large amount of hydroxyl groups on its structure, which enables strong inter- and intramolecular hydrogen bonding. Attributable to its properties like low density, biodegradability, sustainability, non-toxic nature, and high elastic modulus and tensile strength, several studies reported that cellulose can substitute non-renewable and non-degradable materials in many applications. One application that uses cellulose as an alternative for non-degradable and non-renewable models is in electronic devices. The electronic device usually uses polymer synthetic and inorganic materials that are difficult to recycle or decompose. Therefore, it causes serious environmental pollution and increases the petrochemical resources consumption. Cellulose is compostable, so it is expected to eliminate environmental issues [2–4].

Electronic devices can deliver an electric current known as electrical conductivity. However, cellulose is not a good electricity conductor. It can become conductive by combining and introducing conductive materials in its framework. Several methods are in-situ polymerizing the conductive polymer on the matrix of cellulose, carbon nanotubes (CNTs) mechanical-blending and combining with a conductive metal particle in composite or film such as silver nanowires (AgNWs), nickel, and copper [3–5].

Conduction materials' properties depend on electron mobility. An organic polymer such as polyaniline, polyacetylene, polypyrrole, and polythiophene can act as a conductive polymer since its electrons can move freely in the extended π -orbital system along the conjugate backbone [4, 5]. These polymers were employed to prepare sensors and light-emitting diodes (OLEDs), primarily because of features such as low density, photonic properties, special electrochemical, and corrosion resistance. Nevertheless, the weakness of this conductive polymer is difficult to manufacture when applied to the electronic device. To solve this limitation, cellulose, which has good mechanical properties and is easier to form film, can be mixed with a conductive polymer. Moreover, since cellulose contains a large amount of hydroxyl-based groups in its structure, it has good affinities with other polymers, especially conductive polymers. Cellulose could make a conductive polymer easier to manufacture. The application of conductive polymers as a conductive agent as

well as cellulosic type of material in the electrically conductive film preparation or composites has been investigated in recent works [4, 6]

Among the conductive polymers, polyaniline can be applied for solar cells, batteries, semiconductors, etc. Polyaniline is increasingly in demand by researchers because of its low cost, ease of synthesis, and chemical and thermal stability [6]. A study on producing high conductivity cellulose network/polyaniline composite was successfully carried out. This composite was obtained using a new procedure that integrates wood chemical fractionation and polymerization of aniline (in-situ) in purified wood. The fractionation process left the cellulose network intact in the purified wood, and most hemicellulose and lignin were removed. Therefore, the chemical fractionation can improve the wood purified porosity and microstructure obtained. This data was studied by employing the Brunauer–Emmett–Teller (i.e., BET) pore volume and surface area. The comparison of the BET surface area between the wood and cellulose network showed 0.17 and 3.00 m² g⁻¹; while the pore volume showed 0.16 and 2.72 cm³ g⁻¹. Moreover, the increased porosity of purified wood allows the aniline to deeply penetrate, and the polyaniline deposition is uniform in the material microstructure and generates a high conductivity peaking at about 36 S cm⁻¹ [7].

A study about the influence of different cellulose sources on the electric conductivity of cellulose–polyaniline composites was carried out. It was reported that cellulose has four major types, namely cellulose I, cellulose II, cellulose III, and cellulose IV. These types rely on the origin and preparation methods. In correlation with the study on cellulose–polyaniline composite, cellulose II is the most widely used in this application. Cellulose II can be obtained from cellulose I by mercerization or regeneration, where all chains are in a regular parallel arrangement. Cellulose I as the natural cellulose form is the most abundant and important crystalline cellulose form. Cellulose I can be extracted from biomass such as plant cell walls, algae, and from fungi, bacteria, and tunicates [8, 6]. A previous study reported that bacterial cellulose (BC) is frequently used for cellulose–polyaniline preparation [9–12]. Nanocomposites that are flexible electrically conductive from polyaniline and bacterial cellulose have been successfully synthesized (in-situ) using oxidative aniline polymerization utilizing an oxidant from ammonium persulfate (Fig. 1).

FTIR spectra showed that acid addition successfully activated the bacterial cellulose and broke the intermolecular hydrogen bands of BC. Therefore, more hydroxyl groups can be accessed to generate a dispersion of polyaniline within the nanofibrous membrane. According to the SEM, data showed the polyaniline particle was uniformly placed on the surface of the BC fiber and generated a nanosheath with a 200 nm diameter by following along the bacterial cellulose template, as shown in Fig. 2.

The process was controlled by variation reaction time and the proton acid used. The increased reaction time at 30–90 min showed the increased amount of polyaniline and the composite's conductivity. However, the decrease in conductivity at over 90 min is due to the precipitation and aggregation form of the polyaniline particles. The maximum electrical conductivity was reached at a reaction time of 90 min and amounts to 5.0 × 10⁻² S cm⁻¹. The acid used also influenced the composite's

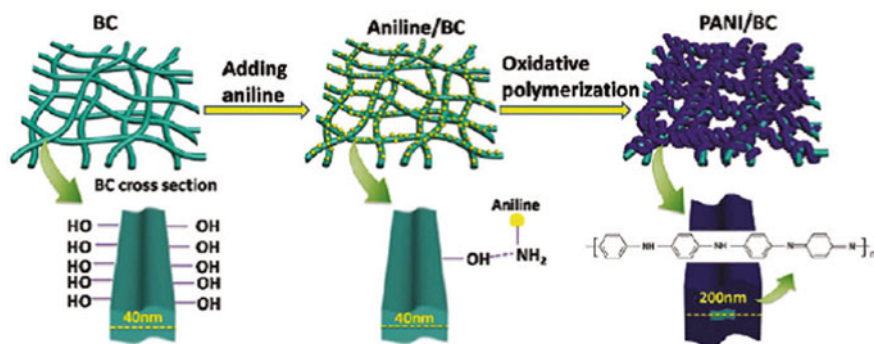


Fig. 1 Schematic diagram of the formation of PANI/BC nanocomposites. Reprinted with permission from [10]. The Journal of Physical Chemistry B Water, 115, 8453–8457. Copyright © 2011 American Chemical Society

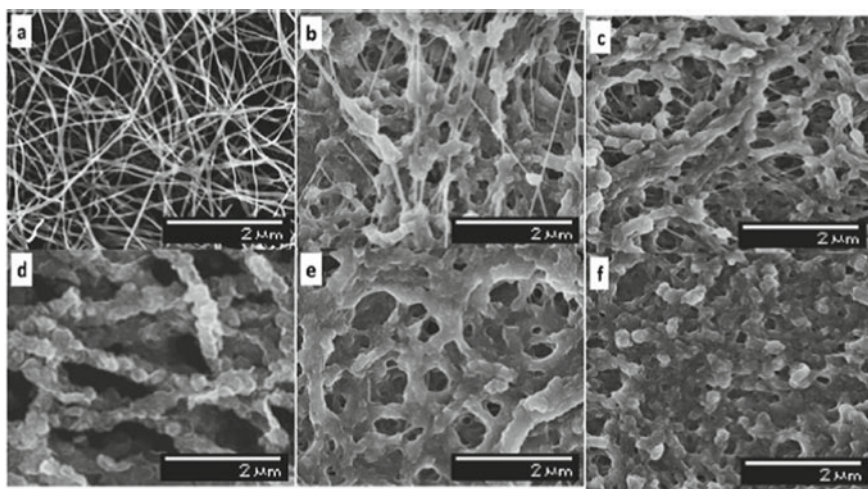


Fig.2 FE-SEM images of **a** pure BC and the PANI/BC composites formed with the reaction time of **b** 30 min, **c** 60 min, **d** 90 min, **e** 120 min, and **f** 180 min, respectively. Reprinted with permission from [10]. The Journal of Physical Chemistry B Water, 115, 8453–8457. Copyright © 2011 American Chemical Society

conductivity and revealed various values. The stronger protonic acid showed higher conductivity [10].

Additionally, research has been conducted on the effect of BC matrices processing methods and synthesis conditions on the synthesis of BC/polyaniline blends. The various matrices were processed by draining, freeze-drying, and regenerating, while the various synthesis conditions included ex-situ and in-situ polymerization. The oven dried-BC was produced by drying the BC membrane in a 400 °C oven. The drained-BC was produced by manually pressing to remove 90% of the water content.

The freeze-dried one was obtained by freezing until it reached $-20\text{ }^{\circ}\text{C}$ for approximately 30 min and then freeze-drying. The third technique is BC regeneration. This method is the polar opposite of the previous two. After drying the wet BC membrane at $400\text{ }^{\circ}\text{C}$ and cutting it into small pieces, a specific amount of BC was added to a LiCl 8% (w/v) solution in dimethylacetamide. The mixture was heated in an oil bath at $110\text{ }^{\circ}\text{C}$ for 1 h and then in an ultrasonic bath at room temperature for 1 h, stirring continuously overnight, to obtain a clear viscous solution. The study concluded that the method of processing the BC matrix and the synthesis conditions have an effect on the composite's surface properties and morphology. The Electron Dispersive X-ray spectroscopy (EDX) revealed only two elements in the BC, C and O, whose proportions varied due to the influence of various processing methods on the bacterial cellulose. After polyaniline is incorporated into the matrix, the BC/polyaniline C, N, and O concentrations are also altered. The amount of polyaniline incorporated into bacterial cellulose was predicted to be different as well. It was demonstrated that the various matrix processing methods for bacterial cellulose and polymerization methods have an effect on the surface elemental composition resulting from the arrangement of various polyanilines. The crystallinity of bacterial cellulose and the bacterial cellulose/polyaniline blend is also influenced by the different processing methods and polymerization methods used for BC matrixes. BC matrixes processed via drying methods such as drained-BC and freeze-dried-BC demonstrated comparable crystallinity of 79.2 and 78.4%, respectively. While the regenerated-BC has a lower crystallinity of 47.7%, this may be due to the BC chains rearranging during the regeneration process, resulting in a higher amorphous content. As shown in Fig. 3, when polyaniline is combined with BC, the crystallinity of the blend decreases. This is most likely because the polyaniline breaks the BC bond. Figure 3 demonstrated that the influence of the processing method for BC matrixes was greater than the influence of the polymerization methods. It can be concluded that the difference in blend crystallinity between in-situ and ex-situ polymerization using various BC matrixes is negligible. The crystallinity of different BC matrixes varies significantly, 50.2%, 19.15%, 18.6%, 46.2%, and 53.7% crystallinity of regenerated-BC, drained-BC (in-situ, ex-situ), and freeze dried-BC (in-situ, ex-situ) blends, respectively.

The polymer content of BC/polyaniline blend with different BC matrixes also shows different values. Drained-BC (in-situ, ex-situ) showed lower polymer content than freeze-dried-BC (in-situ, ex-situ). It is probably related to the high porosity and swelling value of the freeze-dried-BC, which initiate higher incorporation yields of polymer content. However, the drained-BC/polyaniline electrical conductivity is higher than other blends. The contrast data indicates that the different BC matrixes caused polyaniline modifications within the orientation of the chain and the molecular weight. While the effect of the polymerization methods showed that blend obtained via in-situ polymerization has higher polymer content and electrical conductivity than blend through ex-situ polymerization, as shown in Fig. 4. From this data, we can observe that BC/polyaniline blend from the drained-BC and preparation through in-situ polymerization has the highest electrical conductivity [9].

Despite BC being frequently used for cellulose-polyaniline preparation, it has limitations for its low yield. Therefore, the price is more expensive, it takes a long

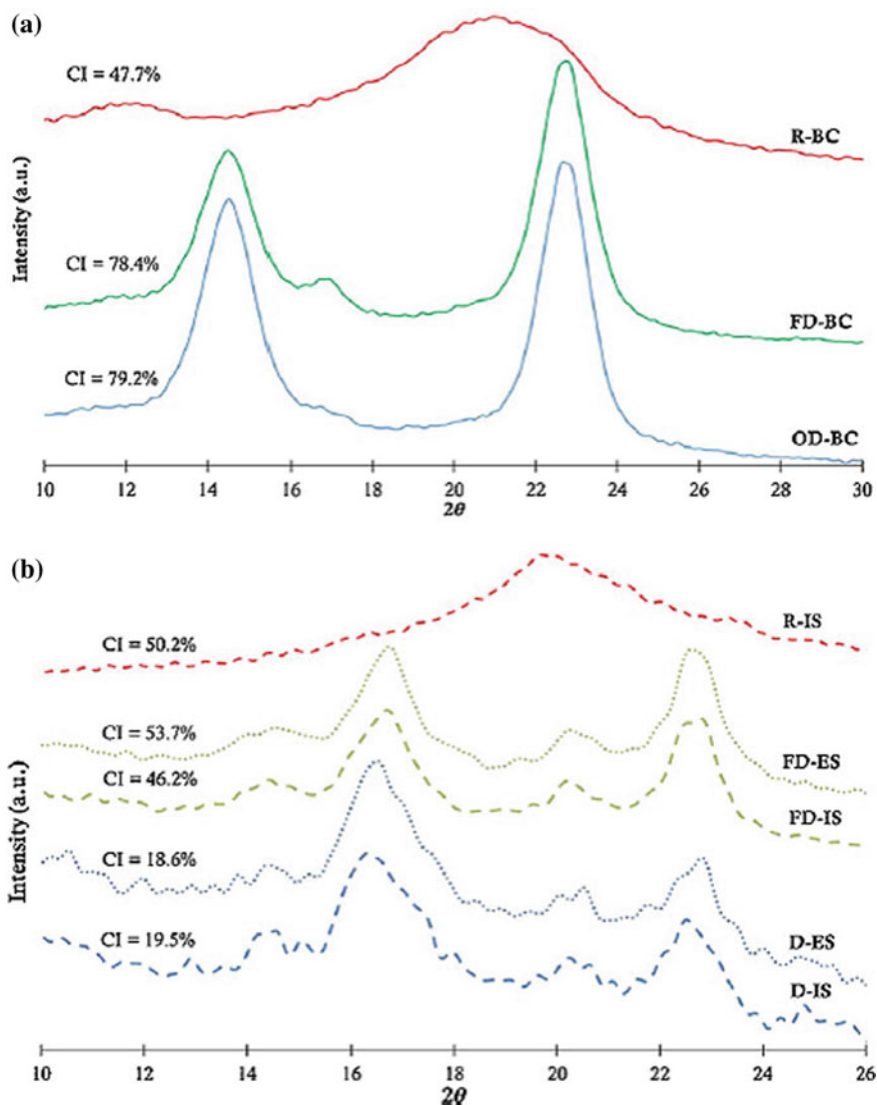


Fig. 3 XRD profile and crystallinity indexes of the **a** BC matrixes and **b** BC/PANi blends. Reprinted with permission from [9]. Carbohydrate Polymers 183 (2018) 254–262. Copyright © 2017 Elsevier Ltd. All rights reserved

time for development, and is difficult to maintain the production environment. Due to these reasons, the production at industries is limited. Apart from this, cellulose I from the plant is very abundant. Many studies about the preparation of cellulose–polyaniline composite from this type of cellulose have also been conducted. However, research about the influence of cellulose I origin is lacking. Hajlaoui et al.

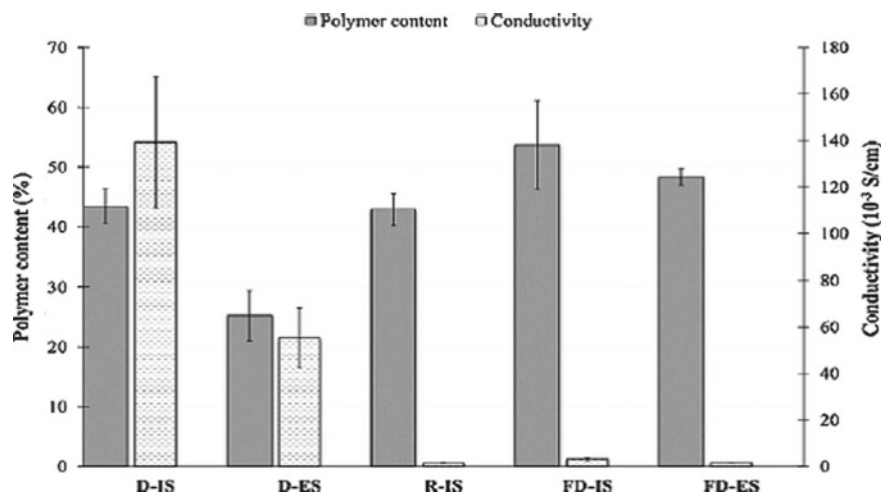


Fig. 4 Polymer content and electrical conductivity of the BC/PANi blends. Reprinted with permission from [9]. Carbohydrate Polymers 183 (2018) 254–262. Copyright © 2017 Elsevier Ltd. All rights reserved

[6] studied the effect of the characteristics of different cellulose sources on the heat stability and electric conductivity of cellulose–polyaniline. The different cellulose sources are cotton, wood, and microcrystalline cellulose. The preparation of its cellulose–polyaniline composite was carried out via polymerization (in-situ) of aniline within the suspension of cellulose. This study showed that the cellulose from different sources has different characteristics in terms of morphology, chemical composition, the total charge of the cellulose, DP, particle size, and crystallinity. Among these characteristics, the crystallinity of pristine cellulose strongly influenced the mass polyaniline loading and influenced the composite electrical properties. Although the three of cellulose types are the same type, i.e., cellulose I, the polyaniline amount in the composite is different. This can be seen from the percentage of nitrogen in correlation with the index crystallinity of cellulose. Different nitrogen amounts in cellulose–polyaniline composite predict the differences of polyaniline integration into cellulose. The result shows that the crystallinity of cotton cellulose (CC) is highest, followed by microcrystalline cellulose (MCC) and wood cellulose (WC). In line with this, the highest amount of polyaniline was also generated by CC-polyaniline composite, followed by MCC-polyaniline and WC-polyaniline, as shown in Table 1. The relationship between the crystallinity of cellulose and the amount

Table 1 Correlation between crystallinity index and nitrogen content [6]

	CC	MCC	WC	CC-PANI	MCC-PANI	WC-PANI
Crystallinity index (%)	89	75	67	73	60	56
Nitrogen content (wt.%)	–	–	–	22.9	19.7	17.8

of polyaniline loading can be explained if the adsorption of aniline is carried out on crystalline cellulose type of domains. Thus, it appears as though aniline adsorption on crystalline cellulose domains prior to polymerization is critical for the aniline polymerization reaction. The electrical conductivity of all composites with varying cellulose sources was found to be proportional to their crystallinity and polyaniline content. The maximum electrical conductivity was demonstrated by the CC-Polyaniline composite, which included the highest amount of polyaniline, followed by the MC-polyaniline and WC-polyaniline composites. These composites have an electrical conductivity of 7.3×10^{-3} , 1.8×10^{-3} , and $1.0 \cdot 10^{-3}$ S/cm, respectively [6].

2.2 Starch

Starch is made up of long simple amylose and amylopectin chains with 1,4- and 1,6-O-glycosidic linkages. Starches are found in a variety of foods, including cassava, potatoes, wheat, rice, and corn. Starch is a readily accessible biopolymer, both in terms of raw material sources and extraction methods. Numerous advantages exist for starch, including its availability, renewability, nontoxicity, and biodegradability. As a result, electronic materials derived from starch are identified as viable renewable alternatives for future electronic device applications in light of environmental concerns. Additionally, starch exhibits swelling and gelation properties, making it an ideal material for active electrodes, boosting loading capacity, reversible discharge capacity, and Coulombic efficiency [13]. Nonpolar solvents are typically employed in the fabrication of organic electronic devices. The polarity of starch renders it incompatible with nonpolar solvents and thus resistant to them, which is critical in the organic electronic manufacturing process [14]. Coating and printing procedures are advantageous for developing inexpensive, large-area, and flexible bioelectronic devices [2]. Starch has been used as disposable organic electronics [14], an electrolyte [15], supercapacitor [16], double-layer capacitor [17], supercapacitor electrolyte [18], and lithium-ion batteries [19]. Additionally, an investigation of the electrical behavior of a SnO₂ hydrosol/starch composite material was conducted [20]. Jeong et al. [14] described a starch paper material for disposable organic electronics that was not planarized or chemically modified. The results demonstrate that starch paper can be bent and has an optical transparency of greater than 93%, making it suitable for flexible and optoelectronic applications [14].

Nanotechnology has made important contributions to the advancement of the electronic research area, particularly batteries and supercapacitors. Supercapacitors have been classified as double-level electrical capacitors and pseudo-capacitors in the charging storage system. The development of supercapacitors is contingent upon the development of electrodes. Starch molecules can act as a green capping material. The effect of starch content on manganese oxide nanostructured growth has been investigated. The results indicate that increasing the starch concentration results in a

decrease in the dielectric constant. Due to the significant influence of starch, homogeneous Mn₃O₄ nanoparticles grow at low temperatures and have a narrow bandgap, making them suitable for lithium-ion batteries [19]. The use of starch as a carbon source was investigated in order to synthesize porous carbon nanosheets for a Zn-ion hybrid supercapacitor. The resulting porous carbon nanosheets cathode exhibits superior electrochemical performance in terms of reversible specific capacity, rate capability, long-term cycle stability, and energy-power densities for Zn-ion hybrid supercapacitor [16].

Researchers have developed an interest in materials with a high dielectric constant as a result of the rapid development of electronic devices and their potential applications in capacitor and memory devices. Polymers, in general, have a low dielectric constant and are, therefore, unsuitable for capacitive device applications. Their dielectric characteristics can be increased by infusing the polymer with conductive material. The dielectric characteristics of biocompatible starch/reduced graphene oxide nanocomposites have been investigated utilizing an aqueous casting process. The results demonstrate that incorporating reduced graphene oxide into a polymer matrix greatly reduces grain boundary resistance, increases the capacitive element, and improves the dielectric constant and AC conductivity of the resulting nanocomposites. The enhanced conductivity and dielectric behavior are a result of the nanocomposites' shorter relaxation time and bulk resistance due to the integration of reduced graphene oxide [1].

The use of biopolymers as anodes in lithium-ion cells is because they are non-toxic, biodegradable, have a high specific capacity, and have good cycling qualities [21]. Starch's swelling, gelation, and retrogradation properties enable it to be employed as an active electrode material, resulting in enhanced loading and reversible discharge capacity, as well as Coulombic efficiency [22]. The anode materials used in lithium-ion batteries determine their storage capacity [23, 24]. The use of starch as an electrolyte is advantageous due to its excellent thermal properties, adhesion, biocompatibility, solubility, and capacity to form films [25]. Pięłowska et al. [13] investigated the physicochemical parameters of starches and their effect on electrochemical qualities. The goal of this research is to determine the effect of the physicochemical properties of various unmodified starches used as active electrode materials on the electrochemical characteristics of lithium-ion cells using biopolymers as active anode materials. The result demonstrates an excellent cycle stability and diffusion coefficient, as well as a high rate capability [13].

Due to its large specific surface area, porous design, and organization with electroactive organic functional groups, eco-friendly porous activated carbon-based electrodes have gained attention. When starch is burned, the -OH group in the starch is released, yielding activated carbon compounds with a high surface area and porosity. Kasturi et al. [17] investigated a porous carbon electrode and biopolymer electrolyte derived from starch for use in a solid-state electric double-layer capacitor. A double-layer capacitor is made of activated carbon and starch. The activated carbon electrode was made using a one-step ZnCl₂ activation technique to obtain porous activated carbon, while the electrolyte film was prepared by solvent casting from starch powder. The graphitization degrees indicate that the higher the concentration of ZnCl₂ in the

starch/ ZnCl_2 composite, the greater the electrical conductivity. Starch/ ZnCl_2 impregnation ratios are 1:1 (Z1), 1:2 (Z2), and 1:3 (Z3). The results of the functional group analysis indicated that oxygen and nitrogen are the major functional groups on the surface of porous activated carbon materials. These functional groups are expected to act as active sites on the conductive carbon surface, adsorbing additional ions from the electrolyte and thereby improving the overall performance of the electric double-layer capacitor. The high nitrogen and oxygen content of the carbon matrix promotes hydrophilicity and wettability, as well as the ability of the carbon matrix to chemisorb ions to and from the starch film electrolyte. Increased conductivity and hydrophilicity of the starch coating contributed to the reduction of resistance and facilitated ionic transport at the electrode/electrolyte contact. Additionally, the XPS data demonstrate the presence of oxygen and nitrogen functional groups on the carbon surface as a result of the inherent oxygen on the carbon surface and the adsorbed oxygen ions in the deficient regions. Following pyrolysis, the nitrogen functional group formed on the Z3 carbon surface by the low surface oxide undergoes structural and electrical modifications, facilitating ion mobility during a redox reaction. Z3 exhibited the least degree of surface oxidation and the highest concentration of nitrogen functionalities, which is expected to result in increased electrical conductivity due to the presence of abundant carbon traces, while the surface nitrogen functionalities act as a support for adsorbing ions during charge storage. Z3 may have an excellent specific capacitance and rate capability for supercapacitor applications, as it is indicated. Z1/starch film/Z1 (Z1-SC), Z2/starch film/Z2 (Z2-SC), and Z3/starch film/Z3 are the configurations of the solid-state supercapacitor (Z3-SC). Due to the fact that Z3-SC exhibits both electric double-layer capacitor and pseudocapacitive behavior, it has a greater specific capacitance. These properties demonstrate increased electrochemical reversibility and redox activity at the electrode–electrolyte interface. The high specific capacitance of Z3-SC is believed to be due to the large electrochemically active surface area created by the electrochemical double-layer capacitance. The large surface area allows for greater charge accumulation. Electric double-layer capacitors offer great power density and fast charge/discharge rates without sacrificing cycling stability. At the high surface area of working electrodes, electric double-layer capacitors store energy electrostatically between the electrode/electrolyte interfaces. The stored energy density in electric double-layer capacitors is dependent on the electrode material's chemical surface characteristics. The carbon electrode facilitates ionic transport, increasing adsorption/desorption and thereby increasing its conductivity. The results indicate that the Z3 electrode is electrochemically active and has the ability to increase the device's capacitance specificity. These favorable electrochemical properties are also a result of the starch film biopolymer electrolytes' quick ion transport capability. Almost all supercapacitors demonstrated a quasi-isosceles triangle shape behavior, a characteristic combination of electric double-layer and pseudocapacitive performance. However, Z3-SC has the highest specific capacitance when compared to Z1-SC and Z2-SC, owing to the Z3 electrode's high surface area and porous design. The high nitrogen concentration of the Z3 electrode helps in the creation of additional active sites for the ions, resulting in a larger capacitance at a lower current. Additionally,

the galvanostatic charge/discharge profile of Z3-SC is investigated at various current densities. Due to the limited diffusion mechanism at the electrode/electrolyte interface, the Z3-SC specific capacitance decreases with increasing current, indicating the material's rapid current response capability and good charge-transfer stability. Electrolytic ions would encircle the electrode/electrolyte contact, resulting in an insufficient amount of time and space for the ions to flow freely. The greater organization of the Z3 material and the starch film electrolyte as an all-solid-state electric double-layer capacitor resulted in a higher specific capacity, energy density, power density, and cyclic stability [17].

2.3 Chitosan

Chitosan is a biopolymer derived from partially or fully deacetylated chitin and composed of a copolymer with N-acetyl-D-glucosamine as well as D-glucosamine attached through β (1–4) chains. Chitosan has several advantages such as biodegradability, biocompatibility, and antimicrobial activity and is also easily processed into various forms [26]. In the electronics field, chitosan has been applied as a type of electrolyte in electric two-layer capacitors [26], for two-layer capacitors and proton battery models [27], for electrolyte for supercapacitors [28], as well as for electrodes for supercapacitors and sensors [29], an electrolyte for electric double-layer capacitors [30]. The use of chitosan which is composited with cellulose has been used to increase the dielectric constant [31]. Generally, supercapacitors' performance is influenced by electrodes and electrolytes as well as device configuration. The electrolyte is one of the components that has an impact on the cycle life, electrochemical potential window, and supercapacitor safety. Chitosan has a low proton and ionic conductivity, so it must be modified to increase its ionic conductivity. Carboxylated chitosan has been applied as a polymer electrolyte for electronic double-layer capacitors [32] and hydrogel electrolytes in quasi-solid-state types of supercapacitors [33]. Carboxylated chitosan electrolytes can be applied in energy storage equipment.

Bonardd et al. [31] produced biocomposites between chitosan with nitrile-modified cellulose nanocrystals. Cellulose nanocrystals were chemically modified with CN groups of acrylonitrile and incorporated into the chitosan matrix. Nanocrystal modification was done to increase the dielectric properties. The increase in the dielectric constant is because of the high nitrile group moment dipole. The dielectric constant improves with the increase of modified cellulose nanocrystals in the biocomposite. Due to the good interfacial polarization and electrode effects, all biocomposites exhibit a large increase in dielectric constant value at low frequencies. The higher the concentration of concentration-modified cellulose nanocrystalline in the biocomposite, the greater the rise in dielectric constant value. However, when frequency increases, the dielectric constant drops in value (Fig. 5). When the frequency of the electric field is raised, the effect of polarization on the dielectric constant is lessened because the polarization mechanism is unable to keep up with the higher electric field frequency [31].

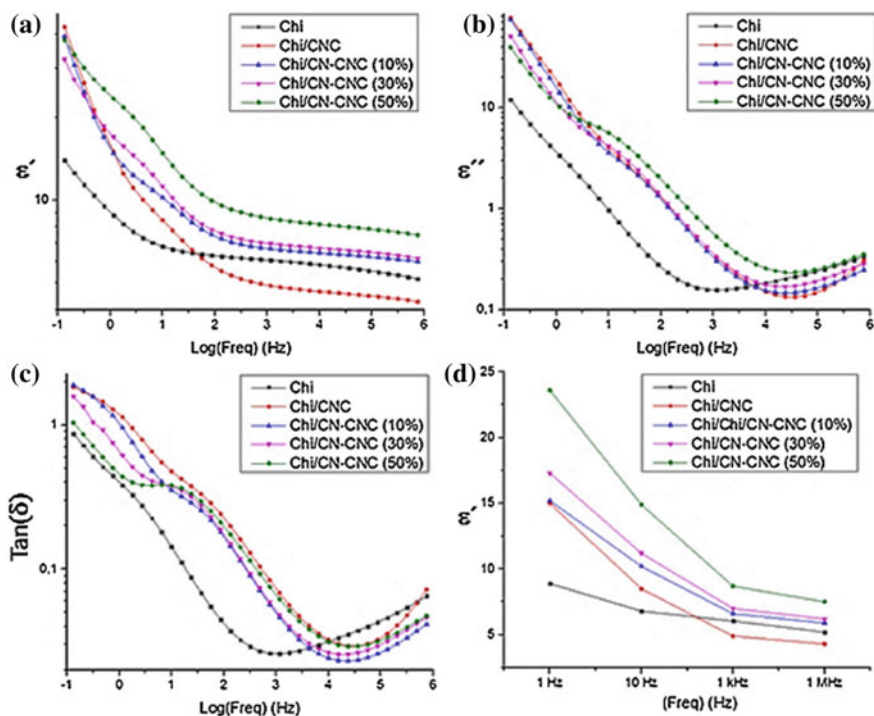


Fig. 5 Evolution of **a** dielectric constant; **b** dielectric loss factor; **c** tan with frequency for pure chitosan, for the nanocomposite with unmodified CNC, and for those with different Cn-CNC amounts; and **d** dielectric constant values at different frequencies for all samples analyzed. Reprinted with permission from [31]. Carbohydrate Polymers 199, 20–30. Copyright © 2018 Elsevier B.V. All rights reserved

Zhang et al. [28] investigated an alkali-tolerant polymeric gel electrolyte membrane for supercapacitors based on cross-linked carboxylated chitosan. Graft copolymerization and crosslinking techniques were used to create an alkali-tolerant hydrogel electrolyte membrane for electrolyte ion movement. The membrane so formed is suitable for usage in both neutral and acidic electrolytes. This membrane expands in alkaline environments and contracts in acidic situations [28]. The cuprous oxide nanocube decorated reduced graphene oxide in chitosan matrix was used to improve the electrochemically active electrode material, resulting in a charge storage capacity of 772.3 Fg^{-1} and cyclic stability of 86% after 2000 cycles. This demonstrates that copper and its oxide-modified electrodes exhibited favorable electrical and electrocatalytic properties, hence increasing the rate of heterogeneous electron exchange between the electrode surface [29].

Hamsan et al. [30] investigated electric double-layer capacitors made of plasticized chitosan:MgCl₂-based polymer electrolyte with glycerol as a plasticizer for chitosan. In this investigation, increasing the amount of glycerol supplied increases the DC conductivity value. When a plasticizer interacts with chitosan, it results

in increased free volume, which facilitates ion mobility and flexibility, as well as promotes ion dissociation, increases the amount of free ions, and results in increased conductivity. The material with the best conductivity is then employed as an electrode separator in applications involving electrochemical double-layer capacitors. The results indicate that the biopolymer electrolyte is stable up to 1.83 V and has a specific capacitance of 117 F/g, a resistance of 182 Ω , an energy density of 13.1 Wh/kg, and a power density of 550 W/kg. These findings suggest that the resulting material may be suitable for use in an electric double-layer capacitor [30].

3 Synthetic-Based Biopolymers in Electronics

3.1 *Polylactic Acid-Based Biopolymer*

Poly(lactic acid) (PLA) is a biodegradable polymer derived from renewable plant sources. Its composites exhibit excellent mechanical, optical, thermal, and processability properties. Significant improvements in the mechanical and physical properties of PLA in its composites have been made in terms of stiffness and toughness, electrical conductivity, and thermal stability. Numerous PLA composites have been widely investigated for use as sensors, actuators, microwave absorbers, and electromagnetic materials, among other applications. Several publications describe the use of conductive fillers in PLA composites to create conductive polymeric composites. Conductive fillers such as graphene, graphite, carbon nanotubes, and carbon black have increased in popularity. This is owing to their advantageous qualities like low cost, high thermal conductivity, ease of production, and resilience to corrosive environments.

Xue et al. synthesized highly electrically and thermally conductive PLA composites containing a high proportion of expandable graphite (EG) using a melt blending approach combined with in-situ exfoliation [34]. They examined the influence of expandable graphite (EG) on the electrical and thermal conductivity of PLA/EG composites. As is the case with many polymers, PLA is a non-conductive polymer. The EG presence in the composite resulted in an increase in the electrical conductivity of the composites as the EG loading percentage increased. The addition of EG significantly enhanced the conductivity of PLA, indicating a rapid change from insulator to semiconductor. When the EG loading fraction of 15% was used, the composite conductivity was nearly ten orders of magnitude more than that of pure PLA. This is owing to the increased dispersion of EG in the polymer matrix and the creation of conductive networks during the blending process. After the EG content was increased to greater than 15% by weight, the electrical conductivity of the composites gradually increased. As can be observed from the findings, the threshold is reached at a graphite concentration of 11.9 weight percent. The gradual increase in conductivity from the value of composites above 15% is due to the interconnecting routes generated by the exfoliated graphite and the more compact structures of the conductive

filler. Thermal conductivity of PLA/EG composites increased with increasing the EG content up to 70% wt. The thermal conductivity of the composites improved significantly when the EG content was greater than 15% wt. At first, conductivity increased slowly at low EG loading. This is due to the fact that exfoliated graphite forms fewer interconnecting networks and the polymer matrix has a high resistance. When the EG concentration was increased to 15%, the high expansion ratio of the EG resulted in the creation of heat conductive networks. According to the findings of this study, the creation of the conductive network in the PLA/EG composite from the in-situ exfoliated graphite flakes may be a significant contributor to the composites' improved conductivity capabilities. Thus, the compact structure of the conductive filler is critical in determining the conductivity of the PLA/EG composites.

As with the previous study group, Mortazavi et al. investigated the thermal reinforcement of PLA via increased graphite addition [35]. They studied empirically and theoretically via multiscale modeling simulations. They began by assessing the conductivity tensors and stiffness of the EG using molecular dynamics models. The example system was developed by a comparison of simulation and experimental results available in the literature. The findings were highly congruent. Finally, this group developed 3D finite element models to determine the heat conductivity of nanocomposite structures. The comparison of experimental and modeling estimates of the thermal conductivity of PLA/EG demonstrates that the thermal conductivity of the nanocomposite is exaggerated (Fig. 6). This is to be expected, as the thermal

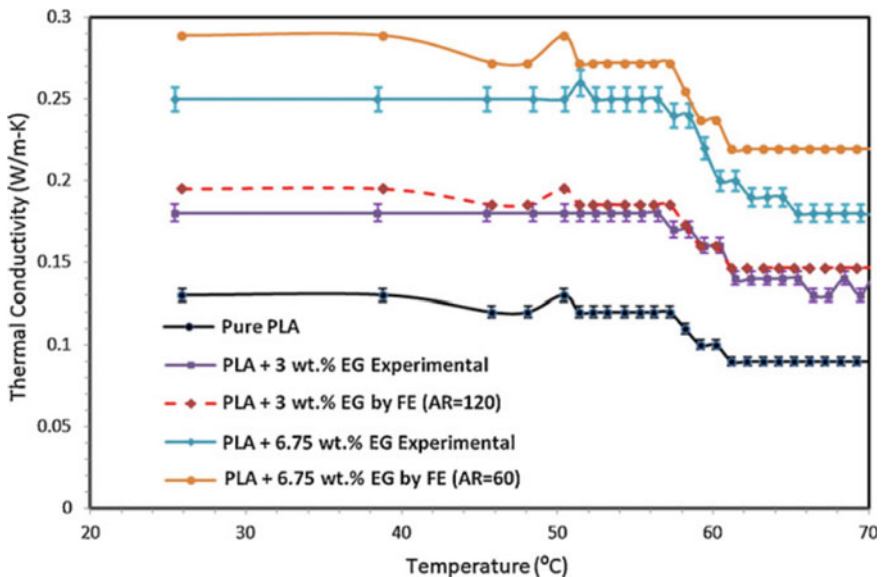


Fig. 6 The thermal conductivity from the nanocomposite with the concentrations of EG at 3 and 6.75 wt.%. Reprinted with permission from [35]. *Thermochimica Acta*, 552, 106–113. Copyright © 2012 Elsevier B.V. All rights reserved

conductivity of graphene is more susceptible to chemical flaws and doping than its mechanical properties. Thus, molecular dynamics simulations may provide a solution to this problem.

In contrast to the previous study group, Kim et al. investigated PLA-based nanocomposites including graphite nanoplatelets derived from exfoliated graphite (EG) in order to attain high electrical characteristics [36]. They generated EG constituted of disordered graphite nanoplatelets via acid treatment and rapid thermal expansion of crystalline natural graphite (NG) and then used melt compounding to synthesize PLA/EG nanocomposites. Additionally, PLA/NG composites were made for comparison. To investigate electrical characteristics, graphite was added to the composites. PLA's electrical resistivity was determined to be in the range of $1016 / \text{cm}^{-1}$. For PLA/NG composites, the value remained constant up to 5% wt. NG and declined slightly with increasing NG loading. When the NG content was 15%, it achieved a value of $107 / \text{cm}^{-1}$. While the electrical resistance of the PLA/EG nanocomposite reduced significantly when the EG content was increased from 3 to 5 weight percent. This composition represents the electrical conduction threshold for graphite nanoplatelets of EG embedded in the PLA matrix. This low graphite concentration for the electrical percolation threshold of PLA/EG nanocomposites is due to the fact that graphite nanoplatelets from EG were distributed uniformly in the PLA matrix, in contrast to the PLA/NG composites. It is worth noting that the electrical resistivity of PLA/EG nanocomposites is around $106 / \text{cm}^{-1}$, which is sufficient for thermoplastics, fibers, and films to achieve electrostatic dissipation. This considerable reduction in electrical resistance is attributed to the clustering of graphite nanoplatelets.

While other groups researched the integration of graphene into PLA, Shen et al. investigated the incorporation of graphene oxide (GO) into PLA [37]. Graphene was produced via ultrasonic exfoliation of graphite oxide and chemical reduction of the graphene oxide that resulted (GO). Preparations were made for the GO samples. rGO-p is the chemically modified GO with polyvinylpyrrolidone (PVP). rGO-g is the abbreviation for glucose-reduced GO. While rGO-t refers to material that has been thermally treated in a vacuum oven. Electrical conductivities of the derivatives of GO were found to be greater than those of native GO. As illustrated in Fig. 7, the conductivity of rGO-g, rGO-t, and rGO-p is 2.5×10^3 , 2.8×10^{-1} , and 1.3×10^{-6} S/m, respectively, which is much larger than the conductivity of GO (2.3×10^{-7} S/m). The fact that rGO-t is less than rGO-g indicates that thermal reduction at 210 °C is insufficient. This could be due to the presence of oxygenated compounds and the resulting smaller sp^2 domains after heat reduction. As a result, restoring the conductivity network in decreased graphene is challenging. Additionally, chemical modification, rather than heat reduction, can be used to create larger GO sheets that are advantageous for electrical conduction. When incorporated into PLA, the native GO and its derivatives produced a range of conductivity values. PLA in its purest form is an insulator with a conductivity of 10–15 S/m. Compression molding demonstrates the effect of heat reduction components in PLA/GO composites, as native GO is not a conductive filler. With the addition of 2% GO, the composite

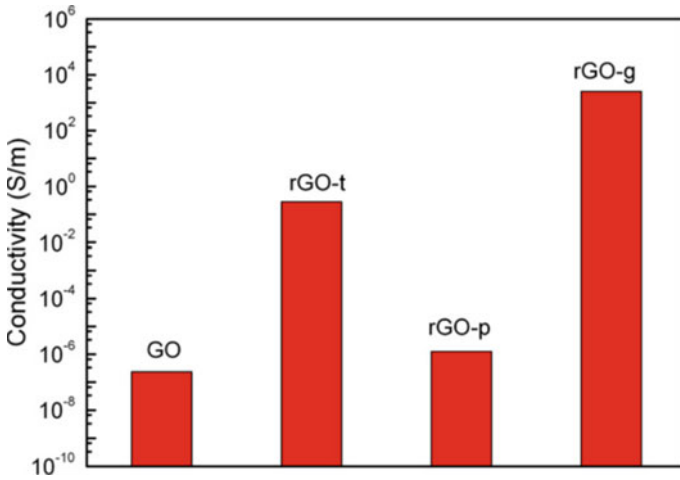


Fig. 7 The electrical conductivity of GO, rGO-t, rGO-p, and rGO-g composite films. Reprinted with permission from [37]. *Composites Science and Technology*, 72(12), 1430–1435. Copyright © 2012 Elsevier B.V. All rights reserved

exhibits a conductivity of around 10^{-4} S/m, which is comparable to the conductivity of PLA/filler composites (Fig. 8). In comparison to PLA/GO composites, the increased electrical conductivity of PLA/rGO-g and PLA/rGO-p is a result of a combination of thermal and chemical reduction of GO. Because the PVP decrease

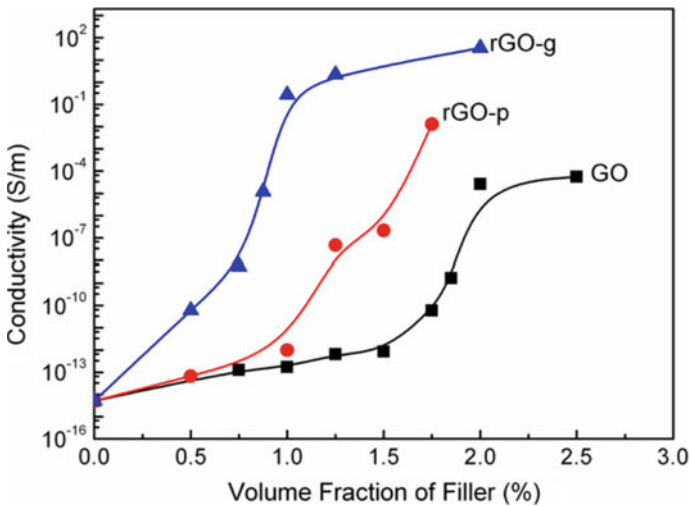


Fig. 8 The electrical conductivity of PLA composites containing GO, rGO-p, and rGO-g. Reprinted with permission from [37]. *Composites Science and Technology*, 72(12), 1430–1435. Copyright © 2012 Elsevier B.V. All rights reserved

is limited in the PLA/rGO-p composite, the high conductivity is attributed to the improved dispersion and exfoliation of rGO caused by PVP. It made use of the network formation of the PLA matrix's interconnecting conductors. According to the literature review, the high electrical conductivity of the PLA/rGO-g composite at a low rGO-g concentration of 1.25 vol. percent was preeminent in the conductivities of the disclosed polymer/graphene composites.

There have been various publications on the use of carbon nanotubes (CNT) as a conductive filler in PLA. Antar et al. developed a bio-based alternative to thermal solar absorbers employing polymers such as polylactic acid (PLA) and polyamide 12 (PA12) Zied [38]. Thermoplastic polymers PLA and PA12 were chosen for their thermoplastic characteristics. While carbon nanotubes (CNT) were chosen to improve the composite's thermal conductivity. At room temperature, the volume resistivity of the conductive composites was determined using a two-probe approach. At the same filler content, the obtained percolation thresholds were 0.5 for PA12 and 0.58 for PLA. This demonstrates that the PLA matrix forms the CNT network more efficiently than the PA12 matrix. As a result, the saved and lost energy increased. Thermal conductivity of the PLA/CNT composite increases by 85% from 0.15 to 0.28 W/m.K when CNT is added at 5% by weight. While PA12 using 5% carbon nanotubes demonstrated a 24 percent increase in power density from 0.21 to 0.26 W/m.K. The difference could be explained by PA12's higher initial thermal conductivity and the denser CNT network in the PLA matrix. Thus, this study demonstrated that the PLA/CNT conductive composite may be a viable candidate for thermo-electrical applications that demand low heat conductivity and high electrical conductivity.

Another work conducted by Antar et al. examined the use of conductive composites as thermoelectric materials for energy harvesting [39]. They filled the composites with a variety of materials, including carbon nanotubes (CNT), expanded graphite (eGR), and a combination of the two. Electrical conductivity-wise, all fillers result in an increase in CPC. However, the combination of carbon nanotubes and eGR (hybrid) produced an excellent synergy. When 12–40 vol. percent of hybrid carbon fillers were used, the electrical conductivity of PLA/hybrid composites increased by 16,000 times (Fig. 9a). Thermal conductivity increased in PLA composites with various fillers. This study discovered a significant difference between the effects of CNT (weak) and eGR (strong). With a 40% filler content, the conductive composite of PLA-eGR increased heat conductivity (Fig. 9b). This number was quite high in comparison to the thermal conductivity scale's narrowness. While the PLA/CNT composites increased the filler content by 18 vol. percent, this is still a low number. Thus, the hybrid filler in the conductive composite acted initially like eGR and then like CNTs. This could be because the melt processing process has a tough time connecting the eGR foils with the CNT bundles in the polymer matrix, especially at high loading. Additionally, in comparison to graphite, carbon nanotubes have a considerable nucleating action, resulting in crystallization and separation of the thermal conductive network.

Antar et al. [5] also investigated multiwall CNT (MWCNT) combined with graphite as the filler for the PLA and PA12 conductive composite as the thermoelectric application Zied [40]. They had variations of PA12/MWCNT, PA12/MWCNT/GR,

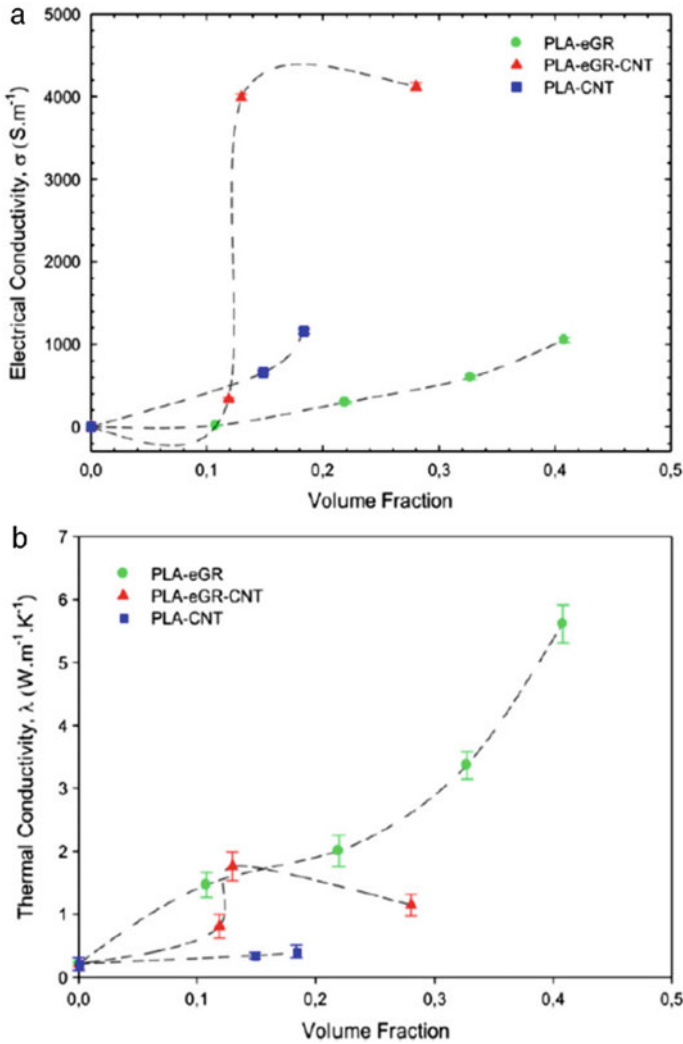


Fig. 9 The electrical **a** and thermal conductivity **b** of PLA/GR, PLA/CNT/eGR, and PLA/CNT composites. Reprinted with permission from [39]. *Materials Letters*, 67(1), 210–214. Copyright © 2011 Elsevier B.V. All rights reserved

PLA/GR, and PLA/GR/MWCNT. The addition of fillers increased the value of electrical conductivity. For the composite of PLA/MWCNT/GR, the addition of fillers from 10 to 30% resulted in the increased value from 116 to 5116 $S.cm$, and for PA12/MWCNT, from 10 to 44 $S.cm$. The PLA/GR composite also had a better electrical conductivity of 32 times with the addition of graphite about 10–40%. In terms of thermal conductivity, there was an increase in the addition of fillers. The thermal conductivity of PLA conductive composite was 3.25

times when using 40% of graphite and 2.3 times when using 30% of MWCNT. However, the PLA/GR composite had a better thermal conductivity compared to PLA/MWCNT/GR composite at the same percentage. This result might be due to the difficulties to achieve the dispersed MWCNT within the polymer matrices. This work showed that electrical conductivity significantly increased with the addition of fillers MWCNT and graphite. While the thermal conductivity relatively remained unresponsive to the addition of the fillers. This characteristic came from the networks in the MWCNT and GR that were thermally disconnected but electrically connected. Therefore, these properties can be adjustable to reach their application as thermoelectric materials.

Raja et al. studied the effect of native and surface-modified carbon nanotubes on the electroactive shape memory properties of PU/PLA blends [41]. Melt mixing was used to create the mixtures. Electrical and thermal conductivity of the PU/PLA mixes improved with the addition of both native and modified carbon nanotubes, as illustrated in Fig. 10. At the same CNT concentration, the inclusion of modified carbon nanotubes significantly improved the electroactive shape memory characteristic of

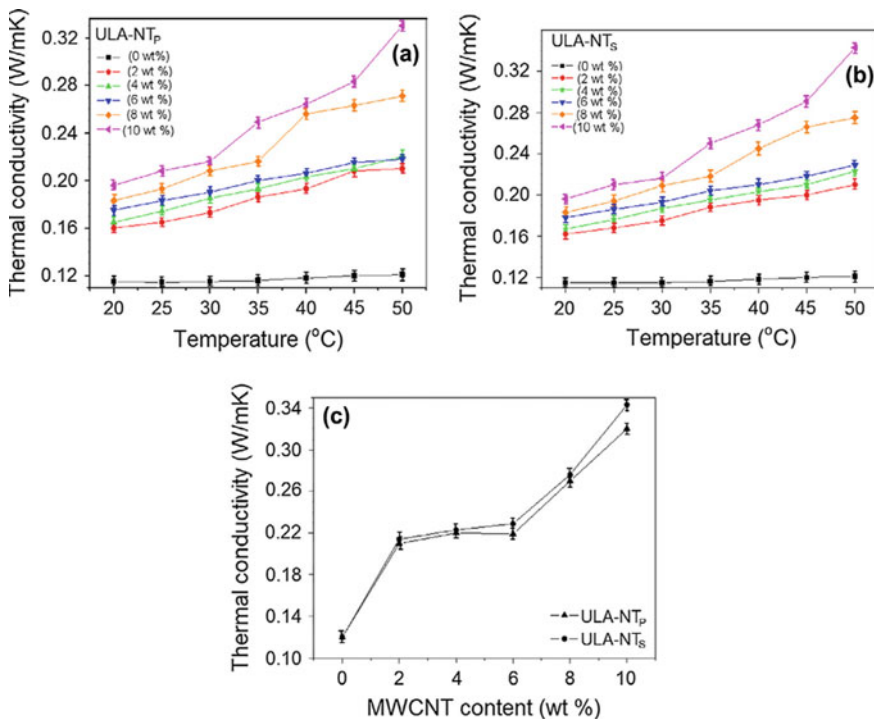


Fig. 10 The thermal conductivity of (i) the PU/PLA/native CNT, (ii) the PU/PLA/modified Fig. 10. The thermal conductivity of **a** PU/PLA/native CNT, **b** PU/PLA/modified CNT, and **c** PU/PLA-PCNT and PU/PLA-SCNT. Reprinted with permission from [41]. European Polymer Journal, 49(11), 3492–3500. Copyright © 2013 Elsevier B.V. All rights reserved

the resulting nanocomposites as compared to the native carbon nanotube composite. This could be owing to the increased phonon scattering caused by the well-dispersed surface-modified carbon nanotubes in the composites.

Lizundia et al. examined the thermal properties of PLA/MWCNT composites, namely the heat capacity, thermal diffusivity, and thermal conductivity [42]. The results indicated that the inclusion of MWCNT increased heat transmission by twofold. Thus, the results demonstrated that carbon nanotubes may be employed successfully to increase the thermal conductivity of PLA. Native PLA has a thermal conductivity of 0.165 W/m K, which is normal for polymers. The inclusion of 3% carbon nanotubes resulted in a significant increase in heat conductivity of approximately 100%. However, adding 0.45 vol. percent of carbon nanotubes decreased heat conductivity by 14%. This is because of the interfacial resistance between the nanotubes and the matrix, which resulted in a decrease in bulk thermal conductivity due to phonon dispersion. Additionally, the arrangement of nanotubes within the polymer matrix had an effect on heat conductivity. At low concentrations, the nanotubes were scattered independently and made little contribution to the conductive channel. As a result, it imparted thermal insulator properties to the composite. While after reaching a critical concentration, the thermal conductivity increased significantly with the addition of nanotubes. In other words, increasing the amount of carbon nanotubes resulted in a network with a larger density of conducting routes, resulting in an increase in thermal conductivity. Then, it is worth noting that the increase in heat conductivity of 100 percent at 3 vol. percent is far greater than that produced by previous polymer/carbon nanotube composites.

The thermal and electrical properties of PLA/MWCNT and PLA/PLA-g-MWCNT composites were examined in the Kim et al. research [43]. Electrical resistivity was decreased when MWCNT was added to the PLA matrix, and this condition continued to decrease as the amount of MWCNT grew (Fig. 11). However, in the composite of PLA/PLA-g-MWCNT, the grafted PLA lowered electrical conductivity by blocking the conductive fillers' direct contact (MWCNT). Thermal diffusivity values for the composite of PLA/MWCNT increased from 0.1 to 0.35 when the MWCNT content was increased from 0 to 1.2%, as shown in Fig. 12. While the thermal conductivity was improved from 0.16 to 0.42, as seen in Fig. 13, the MWCNT content rose from 0 to 1.2 wt. percent. However, when PLA/PLA-g-MWCNT composites were added, the addition of grafted PLA resulted in an increase of 0.41 for the same filler amount.

Li et al. used the casting method to create a conductive biopolymer composite from PLA and carbon black (PLA/CB) [44]. We examined the vapor sensing behaviors of the PLA/CB conductive composite. Their findings indicated that a PLA/CB conductive biopolymer composite could be developed to serve as a more suitable choice for a vapor sensor. By altering the resistance when exposed to organic vapors such as ethyl acetate, ethanol, methanol, xylene, carbon tetrachloride, and n-hexane, the vapor sensing behaviors of the composites were investigated. The configuration

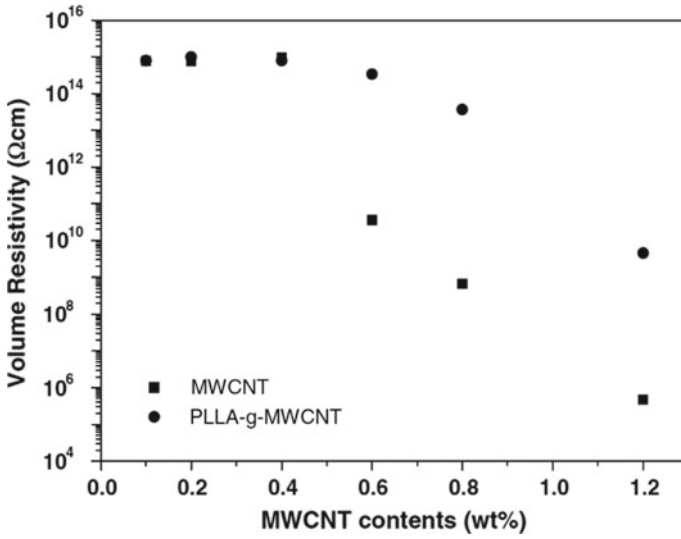


Fig. 11 The volume resistivity for the composites of PLLA/MWCNT and PLLA/PLLA-g-MWCNT. Reprinted with permission from [43]. Current Applied Physics, 8, 803–806 [41]. Copyright © 2007 Elsevier B.V. All rights reserved

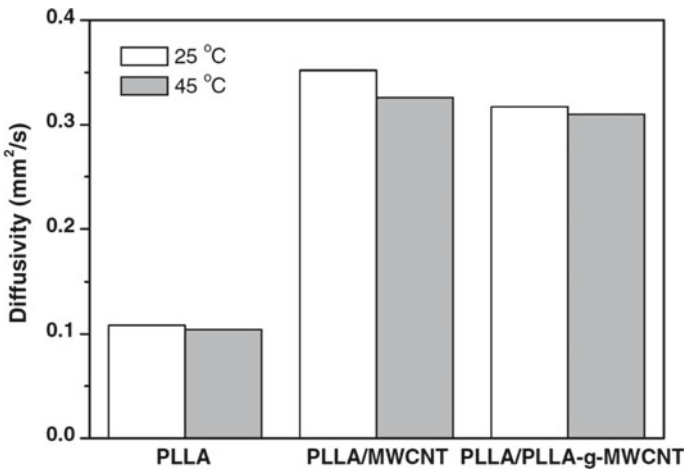


Fig. 12 The thermal diffusivity for the PLLA and PLLA/MWCNT composites. Reprinted with permission from [43]. Current Applied Physics, 8, 803–806 [41]. Copyright © 2007 Elsevier B.V. All rights reserved

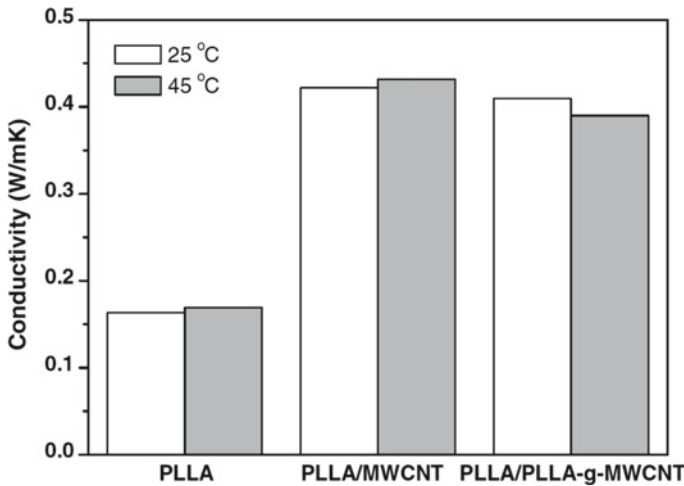


Fig. 13 The thermal conductivity for the PLLA and PLLA/MWCNT composites. Reprinted with permission from [43]. *Current Applied Physics*, 8, 803–806 [41]. Copyright © 2007 Elsevier B.V. All rights reserved

of the CB conductive networks had an effect on the sensory behaviors. In terms of resistivity, increasing the CB content resulted in a decrease in the resistivity of composites. However, when CB loading was between 1.21 and 1.39 vol.%, there was a significant decrease in resistivity. This was proposed as the percolation value based on the creation of CB's conductive network in the composite and the insulator–conductor transition. This conductive network is created when the CB particles come into contact with the PLA matrix. In this study, PLA/CB samples containing 1.39 vol. percent CB were used to investigate vapor sensing characteristics. After 60 s of exposure, the composite's vapor sensing response increased dramatically in solvents such as ethyl acetate, carbon tetrachloride, and xylene. However, for solvents such as ethanol, methanol, and n-hexane, the electric resistance rose only a few times.

Similar to the previous study, Kumar et al. explored volatile organic compound (VOC) sensors fabricated from a PLA/MWCNT conductive polymer [45]. They prepared the conductive polymer by the solution mixing approach. The conductive polymer transducers were made using the layer-by-layer spray process (sLbL). The chemo-resistive properties of the sensors were then investigated by exposing them to organic vapors such as chloroform, methanol, toluene, and water. The results indicated that the molecules exhibited a range of physical properties, including molecular size, solubility, and polarity. The advantages of transducers for chemical vapor sensing are their capacity to discriminate between different types of vapor and their rapid reaction to the vapor itself. When exposed to chloroform vapor, the addition of 2–3% carbon nanotubes to the PLA composite exhibited a substantial vapor

coefficient (PVC) effect. After the vapor is removed, the CPC sensor's resistance returns to its initial value nearly instantly. As a result, this occurrence is reversible and repeated. Additionally, the electrical signal was stable and responsive. In their PVC, the PLA/CNT transducers displayed a distinct pattern. The PVC signal clearly demonstrates the strong affinity of PLA/CNT transducers for chloroform. This could be attributable to the analyte's molecular weight and diffusion coefficient. In terms of selectivity for chloroform and methanol vapors, PLA/CNT transducers, like any other hydrophobic polyester, are more sensitive to chloroform. This occurs as a result of intermolecular interactions. However, the selectivity of the transducer can also be influenced by vapor pressure, temperature, and molecule size. Conductive composites of PLA and carbon nanotubes were extremely selective for chloroform vapor. The selectivity property is a result of the natural interaction between the analyte molecules and macromolecules in the conducting network matrix. Both the vapor profile and the CNT content had an effect on the solubility parameters and percolation theory. The selectivity of PLA/CNT conductive composites for vapors is determined by their solubility. After all, chloroform was the vapor that was driven to the sensors with the highest response capability.

Luo et al. conducted another study on sensors [46]. They simulated the capacitance variation for the fundamental sensor construction consisting of PLA sheets. The thinner the PLA sheets, the greater the change in capacitance caused by deflection. Because the capacitance value was determined analytically, it must be regarded as an estimate. However, due to the high level of interest in the pulse wave shape, the parameter in the sensor characteristic was not deemed a demanding subject.

PLA is a chiral thermoplastic biopolymer. Its derivative, poly-L-lactide (PLLA), has a high piezoelectric characteristic due to its 37% crystallinity. Due to the lower piezoelectric constant of a polymer membrane compared to inorganic piezoelectric materials, the applicability of piezoelectric polymers is limited. The piezoelectric constant increases as the crystallinity and orientation of a polymer membrane increase. Tajitsu et al. used a high-speed spinning method to optimize the crystallinity and ultimately the piezoelectricity of PLLA fiber [47]. When an ac voltage was applied to the resulting PLLA fiber, it was driven by the piezoelectric action. This resulted in the complete bending of the PLLA fiber. This group was successful in capturing a silica bead using a pair of PLLA fibers. This was done with the intention of using the fibers as tweezers for biological cells. This success may result in the product's manufacturing.

Lee et al. studied the piezoelectric characteristics of PLLA fibers using a variety of stacking orders (constructive, destructive, and multi-layered folding) and electrode configurations (series and parallel) [48]. Then, its piezoresponse behavior was compared to that of polyvinylidene fluoride (PVDF). PVDF had the greater peak-to-peak output voltage (V_{p-p}) in the constructive stacking. This is due to the orientation and linear structure of the CF dipoles on the PVDF surface. However, during destructive stacking, the orientation of the C = O dipoles in the helical PLA outweighed

the influence of the PVDF's CF dipoles. As a result, the V_{p-p} value for PLA is increased. While in multilayer stacking, the output voltage was dependent on the number of stacks since the V_{p-p} increased as the number of stacks increased. In terms of electrode arrangement, the parallel connection produced a greater piezoelectric output, and this configuration was successfully applied to the power source to charge a capacitor and run the LED.

To investigate the superpiezo effect in its piezoelectric application, the biopolymer PLA was filled with ceramic barium titanate ($BaTiO_3$) [49]. They used an electrospinning process to produce PLA/ $BaTiO_3$ composites with filler concentrations of 0, 15, and 42%. Their analysis demonstrated that a 42% filler content produced the optimal piezoelectric response. Additionally, this work demonstrated that thin mats (0.15 mm) can alter the behavior of a liquid crystal (LC) when tapped with a finger. This is an intriguing strategy for powering certain liquid crystal displays and other uses.

In another study, electrospun PLA fibers with an average diameter of 2580 nm were used to coat poly(3-hydroxybutyrate) (PHB) nanoparticles [50]. The modification of PHB's surface resulted in the formation of rough surface granules with a topography of 200–500 nm and a crystallinity of approximately 1.8 times. This material exhibited a piezoresponse of three-dimensional scaffolds that aided Soas-2 osteoblast cell adhesion. Additionally, this study shows that it can be used in bone tissue engineering.

3.2 Polyvinyl Alcohol-Based Biopolymer

In addition to the biopolymers mentioned above, multiple synthetic biopolymers have been used for electronic applications, including polyvinyl alcohol (i.e., PVA). PVA is generally a synthetic type of biopolymer that is obtained not via polymerization such as other synthetic polymers, but through polyvinyl acetate (PVAc) hydrolysis. PVA has good thermal and mechanical properties, transparency, and endurance to oxygen permeation [51, 52]. Studies about PVA for the electronic device have been conducted by preparation of PVA composite for example by incorporation with other polymers such as poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate) [53, 54], poly(vinyl pyrrolidone) (PVP) and lithium acetate [55], borax [56], $Cu(NO_3)_2 \cdot 3H_2O$ [57], and Graphite oxide (GO) [58]. PVA has a large number of hydroxyl groups and has good adhesive properties so it will support the easy formation of composite and can promote the purpose of binders in supercapacitor electrodes [54].

One of the interesting materials to be combined with PVA for dielectric and supercapacitor requirements is poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate) (i.e., PEDOT: PSS). PEDOT is conducting polymer which has high electrical conductivity (up to 500 S/cm), good chemical and thermal stability, and is

usually used as organic transistor and OLEDs. Nevertheless, PEDOT itself has a solubility problem so it is difficult for the next process. This problem can be avoided by utilizing a water-soluble polyelectrolyte. The PSS which can act as the dopant of charge-balancing during polymerization can blend with PEDOT to obtain highly stable dispersion in water and, therefore, can improve the processing ease. However, pure PEDOT: PSS obtained is still needed to combine with the PVA to enhance the mechanical characteristics and processing, although it causes the conductivity to decrease [53, 59].

3.3 *Polyhydroxyalkanoates-Based Biopolymer*

Polyhydroxyalkanoates (i.e., PHAs) have attracted considerable attention in business and research due to their biodegradability, piezoelectricity, and thermoplasticity qualities. However, the high expense of manufacturing PHA has sparked interest in locating significantly cheaper basic materials. PHAs have been employed in a variety of applications, including packaging, food, and pharmaceuticals. Additionally, they have been extensively investigated for use in biomedical applications. Numerous profitable and important PHAs are available, including poly(3-hydroxybutyrate) (i.e., P3HB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (i.e., PHBHV), poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (i.e., P3HB4HB), and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (i.e., PHBHHx).

PHB is a thermoplastic polyester that is used to make biodegradable plastics. Numerous bacteria synthesize this polymer as an energy storage material and in the granules that grow inside their cells. Valentini et al. examined the use of PHB in a system that converts mechanical energy to electrical energy via a process called friction charging [60]. They investigated the use of PHB biopolymer as a triboelectric generator (i.e., TEG). The TEG has the potential to be used in self-powered sensors for temperature and environmental monitoring, as well as in large-scale applications. TEG was formed by stacking a drop cast of PHB film indium tin oxides. It was then covered with poly(ethylene terephthalate) (i.e., PET) resin and PET sheet. It generated a 3 V open-circuit voltage and a 3×10^7 mA/cm² short circuit current density. This resulted in a peak power density of 0.01 mW/m² for the corresponding peak power density. This exploratory investigation is part of the process of developing PHB as the primary material for a self-powered bioelectronic. This biopolymer-based TEG was capable of harvesting energy through mechanical deformation and has the potential to be used in self-powered systems for portable electronic devices.

Boutry et al. conducted another study in which they found biodegradable sensor arrays consisting of PHB/PHV [61]. They obtained a pressure response from the biodegradable sensor arrays as a result of their experiment, which was effective in the application of cardiovascular monitoring. The sensor area was defined as the intersection of two orthogonal electrodes. Pressure sensitivity was 0.76–0.14 kPa1 on average for 20 sensors in the low-pressure zone (i.e., $p < 2$ kPa) and 0.11–0.07 kPa1 in the high-pressure region (i.e., $p > 10$ kPa).

3.4 Poly(ϵ -Caprolactone)-Based Biopolymer

PCL is an aliphatic polyester polymer that is completely biodegradable. Due to its strong crystallinity and hydrophobicity, it degrades slowly in the presence of water and is easily produced thermally. PCL is widely used in a wide variety of industries, including biodegradable materials, medication delivery systems, and implantable biomaterials. PCL can be processed using ring-opening polymerization with a variety of different catalysts. To improve the mechanical, thermal, and barrier properties of PCL while preserving a high degree of biodegradability, a variety of nanoparticles have been incorporated into the matrix. Graphene, carbon nanotubes, silica, and clays are all notable nanoparticles.

Fortunati et al. examined the influence of single-walled carbon nanotubes (SWCNTs) and silver nanoparticles (AgNPs) on conductive biopolymer composites [62]. They discovered that AgNP promotes the development of conductive passageways in single-walled carbon nanotubes (SWCNT). Through the solvent casting process, various amounts of SWCNT were coupled with AgNP and incorporated into the PCL matrix. We evaluated the electrical characteristics of binary PCL/AgNP, PCL/SWCNT, and ternary PCL/AgNP/SWCNT composites. Figure 14 illustrates the wide range of conductivity values found in PCL composites. Electrical conductivity rose steadily when the filler content was increased. The PCL/AgNP composites, on the other hand, exhibited poor electrical characteristics. In comparison to both binary composites, the PCL/AgNP/SWCNT composites had a greater conductivity

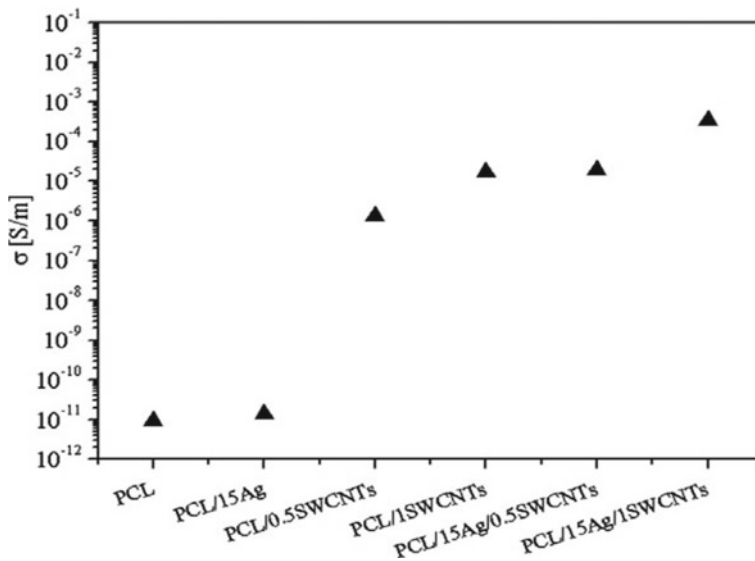


Fig. 14 The DC electrical resistivity from the binary (PCL/SWCNTs, PCL/Ag) and ternary (PCL/Ag/SWCNTs) composites. Reprinted with permission from [62]. Carbon 49(7), 2370–2379. Copyright © 2011 Elsevier B.V. All rights reserved

value. This research has shown that in the presence of SWCNT, Ag nanoparticles enhance the development of conductive pathways. The nanoparticles were unable to form a conductive pattern in the matrix PCL polymer, as demonstrated in this work. As a result, the addition of tiny SWCNT improved the electrical characteristics of PCL/AgNP composites substantially.

Saeed and Park investigated composites of polycaprolactone and multiwalled carbon nanotubes (PCL/MWCNTs) produced using in-situ polymerizations [63]. They looked at the influence of dispersion and purification on the electrical characteristics of MWCNT nanocomposites. Two types of nanocomposites were synthesized: PCL/P-MWCNT and PCL/A-MWCNT. Native MWCNT (P-MWCNT) and purified MWNT were used as reinforcing materials (A-MWCNT). The A-MWCNT was purified using a nitric acid procedure to add carboxyl groups (COOH). Both nanocomposites exhibited remarkable electrical conductivity while containing a little amount of filler. The PCL/P-MWCNT and PCL/A-MWCNT percolation limits were determined to be 2 wt. percent of the MWCNT. This low percolation rate indicated that P-MWCNT and A-MWCNT were well dispersed inside the PCL matrix. With 2% filler, the conductivity of the PCL/P-MWCNT composite increased rapidly and varied between 10⁻¹ and 10⁻² S/cm. While the conductivity of the PCL/A-MWCNT composite grew steadily with filler loading and reached 10⁻² S/cm at 7% filler. For the whole range of MWNT content, the conductivity of the PCL/P-MWCNT was larger than that of the PCL/A-MWCNT. This could be because the acid treatment destroyed the MWNT's p-network. However, it is believed that when the conductivity of the composite originally rose, it was due to the low percolation threshold and excellent dispersion of the fillers inside the PCL matrix.

Sanchez-Garcia et al. examined the use of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) as reinforcing materials in order to improve the thermal conductivity of PCL and polyhydroxybutyrate-co-valerate (PHBV)/CNTS composites [64]. They developed the solvent casting method using PCL and PHBV composites filled with CNT or CNF. This work established that carbon nanotubes and carbon nanofibers can be used to enhance conductivity qualities. When illustrated in Fig. 15, the electrical conductivity of PCL and PHBV nanocomposites rose dramatically as the CNT and CNF concentrations increased. This is owing to the high diffusion of carbon nanotubes and carbon nanofibers as fillers in the polymer matrix. Additionally, this may be related to the percolation threshold. The electrical conductivity of nanocomposites including carbon nanotubes was larger than that of nanocomposites containing carbon nanofibers. Electrical conductivity rose from 2.4 × 10⁻⁶ S/cm with 1% CNT to 0.33 S/cm with 10% CNT in the PCL nanocomposites. When CNF was used as a filler, the electrical conductivity rose with increasing amounts of CNF, reaching 0.10 S/cm at 10% CNF. This behavior was also observed in the PHBV nanocomposites, where the CNT filler had a higher electrical conductivity than the CNF filler. As illustrated in Fig. 16a, the thermal diffusion of PCL composites increased as the CNT and CNF concentrations rose. With 10% CNT concentration

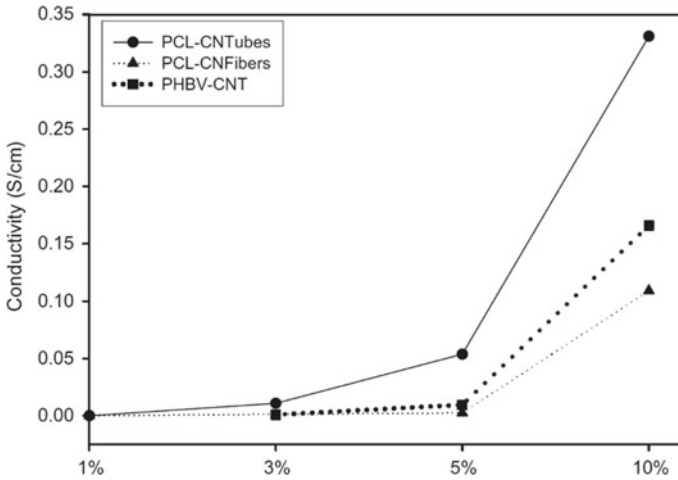


Fig. 15 The conductivity of nanocomposite of PCL and PHBV with 1, 3, 5, and 10 wt.% of CNT and CNF as fillers. Reprinted with permission from [64]. *Composites Science and Technology*, 70(7), 1095–1105. Copyright © 2010 Elsevier B.V. All rights reserved

in PCL nanocomposites, the thermal diffusivity increased by approximately 160 percent compared to 1% CNT content. While for nanocomposites containing CNF, the rise is around 165 percent when the composite contains 10% CNF against 1% CNF. Figure 16b illustrates the heat diffusion of PHBV's CNT and CNF. Thermal diffusion was boosted by 235 percent when 10% CNT and 10% CNF were added as fillers to the PHBV composites. This is because of the thermal transport properties of both fillers, as well as photon diffusion inside the matrix.

4 Conclusion

This chapter reviewed the electrical properties of various kinds of biopolymer matrix fillers and composites. It can be concluded that biopolymers are generally not conductive. The inorganic fillers were combined with the biopolymer matrices to enhance electrical conductivity, which greatly differs from the native biopolymer and demonstrates suitable characteristics. For this purpose, a variety of many types of fillers were investigated. The electrically conductive, safe, renewable as well as biodegradable properties make the implementation of biopolymers in electronics worthy to be further investigated in terms of the production of environment-friendly products.

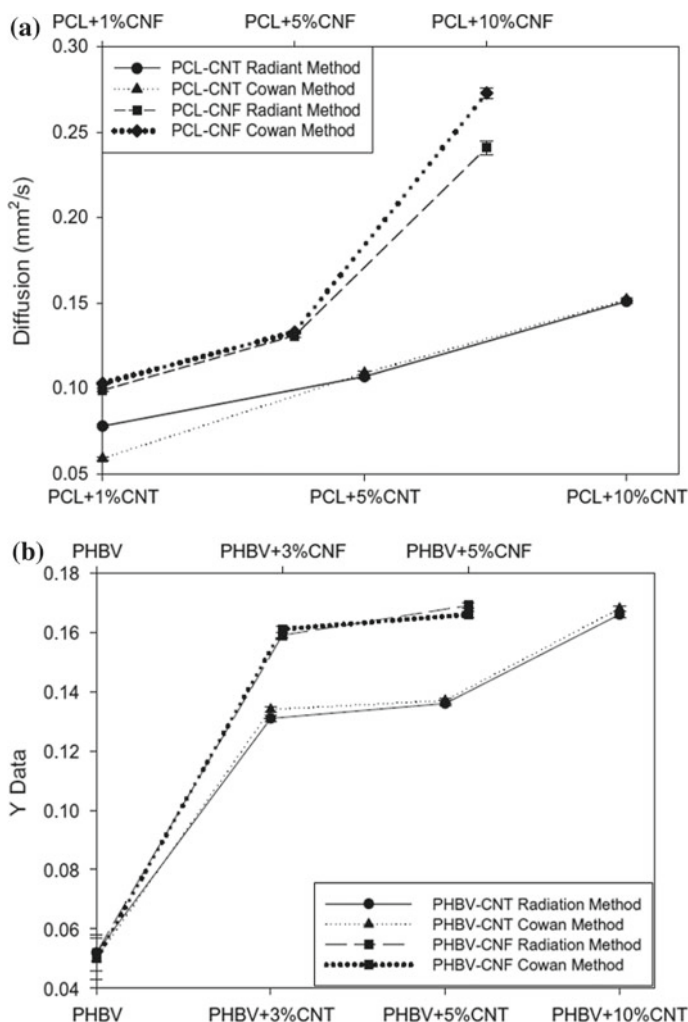


Fig. 16 Thermal diffusion coefficient of **a** PCL nanocomposites with 1, 5, and 10 wt.% of CNT and CNF as fillers **b** PHBV nanocomposites with 1, 5, and 10 wt.% of CNT and CNF as fillers. Reprinted with permission from [64]. *Composites Science and Technology*, 70(7), 1095–1105. Copyright © 2010 Elsevier B.V. All rights reserved

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Biopolymer in Wastewater Treatment



Jasdeep Singh, Shubham Kumar, and Swati Sharma

Abstract Water is the most essential resource on the planet, as it is required for the survival of all living organisms. Apart from the need for water for drinking, it is an essential component of modern societies with agricultural and industrial sectors heavily dependent on it. However, the inappropriate release of a range of harmful organic and inorganic contaminants from untreated industrial, agricultural, and domestic wastewater has a negative impact on water resources and thus poses a great risk to aquatic systems, animal, and human health. Organic toxics like dyes, as well as heavy metals including cadmium, chromium, cobalt, copper, lead, mercury, nickel, tin, and zinc, may be present in our water supplies, posing major health risks to all living species. Some methods, including adsorption, coagulation, flocculation, ion exchange, and membrane filtration, precipitation and co-precipitation, and solvent extraction, have been tested for the removal of these toxic pollutants. However, the capital cost for these treatment methods is very high and require synthetic toxic reagents. Biopolymers have been recently suggested for wastewater treatment because of their renewable properties, sustainability, biodegradability, and non-toxicity. Biopolymers can also be combined with a variety of reinforcing elements (antioxidants, natural fibres, pigments, and micro-, nanoparticles of inorganic fillers) to create unique composites with enhanced characteristics. In this chapter, we describe the application of various natural biopolymers and grafted copolymers to remove heavy metals, dyes, oils, other chemical or drugs, and turbidity from the wastewater, as well as challenges and future perspectives in the development of novel biopolymers.

Keywords Biopolymers · Wastewater treatment · Bio-flocculants · Polysaccharide polymers · Grafted flocculants

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1 Introduction

Annually, almost 140 million tonnes of synthetic polymers, such as plastics, are produced around the world, and contribute to water pollution. Because they are incredibly stable, their degradation being nearly unattainable, the synthetic polymer has been recognised as a major setback for wastewater treatment [14].

Further, the water resources are also polluted with different heavy metals, for example, cadmium, chromium, cobalt, copper, mercury, nickel, lead, and zinc and dyes, [45] which are found in industrial and agricultural effluents and pose substantial health risks to living beings [33].

To remove these toxic chemicals and ions, various technologies have been developed including precipitation and co-precipitation, adsorption, coagulation, flocculation, ion exchange, membrane filtration, and solvent extraction technique. However, the major problem associated with these techniques is the use of synthetic toxic reagents that are again non-biodegradable, moreover, these are costly also and thus have high input costs for treatment [32].

Biopolymers, also called natural polymers, are naturally occurring substances generated by living organisms (plants, animals, bacteria, and fungi) [45] throughout their whole life cycle [50].

Due to the following properties, the biopolymers are considered as an attractive alternative to synthetic toxic reagents for the treatment of wastewater:

- I. Biopolymers are very abundant as well as cheap.
- II. They can be used for the removal of a wide range of contaminants as their adsorption capability can be easily modulated by changing the attached active functional groups, e.g., amino ($-NH_2$) and hydroxyl ($-OH$) groups.
- III. They have diverse applications, in the food, pharmaceutical, and bio-medical industries, attributed to a lot of physical or chemical methods available for their functional modification.

They do not cause any harm to the environment because of their non-toxic, renewable, and biodegradable nature. Only organic wastes like carbon dioxide and water are formed upon biopolymer degradation by naturally occurring microorganisms compared to petroleum-derived plastics having hazardous effects on the environment [32].

Biopolymers can be classified in different ways, for example, based on whether they are natural or synthetic; biodegradable or non-biodegradable; depending on the monomeric units; and source of origin [11, 48] (Figs. 1 and 2 and Table 1).

2 Biopolymers for Wastewater Treatment

Biopolymers being biodegradable and non-toxic substances have been proposed for wastewater treatment owing to their sustainable and renewable properties [30]. Moreover, novel composites with improved properties may be developed by

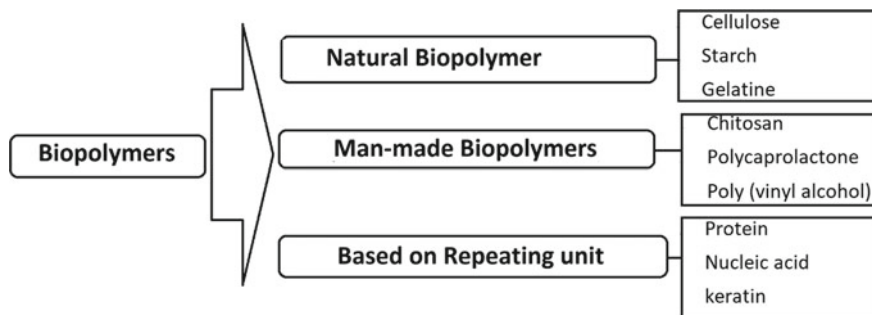


Fig. 1 Biopolymers classification

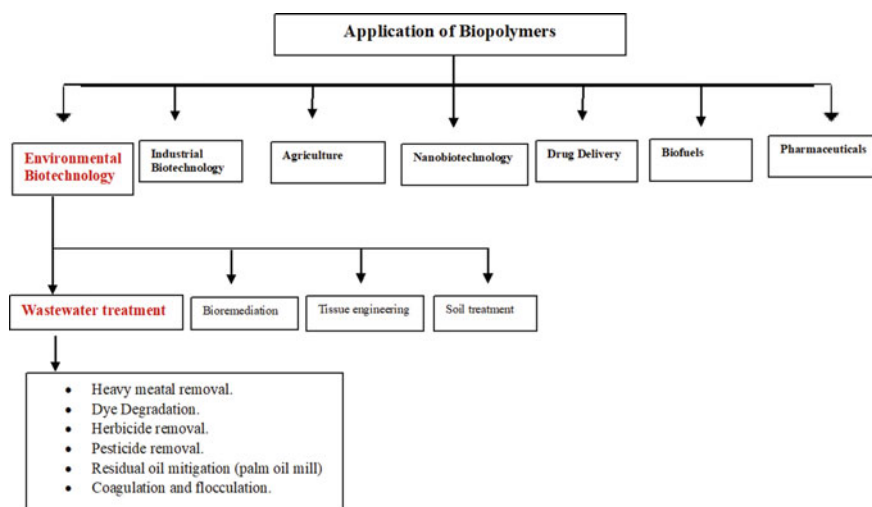


Fig. 2 General application of biopolymers in different fields

grafting biopolymers with various materials such as antioxidants, inorganic nano- or micro-fillers, natural fibres, and pigments [37, 50].

Industrial wastewater contains in large amounts various types of organic and inorganic materials including metals, and hazardous compounds such as fine suspended and dissolved solids. Small particle size and surface charge do not permit finely suspended solids to form heavier aggregates for sedimentation and their removal through filtration is challenging. Residue oil, from Palm oil mill effluent (POME) or vegetable oil mill effluents, is the most important concern in oily wastewaters, and it must be addressed to minimise the formation of interfaces in water-treatment plants, avoid issues in the biological treatment stages, and meet water-discharge criteria. Gravity-based oil separation is challenging and lengthy because emulsified oil droplets do not spontaneously consolidate into bigger flocs [31, 45].

Table 1 Biopolymers and their classification

Biopolymer		Biodegradable Bio-based		Non-biodegradable		References
Microbial origin	Plant origin	Animal origin	Bio-based	Fossil-based		
Alginate	Cellulose	Chitin/chitosan	Polyethene	Poly (alkylene dicarboxylate)	[15]	
Carrageenan	Starch	Nucleic acids	Polypropylene	Poly (glycolic acid)	[49]	
Dextran	Polysaccharides	Proteins	Polycarbonate	Polyphosphazenes	[33]	
Gellan Gum	Tannin	Glycogen	Polyether amides	Polyvinyl alcohol	[34]	
Cellulose	Gums	Glycosaminoglycans	Phenolic resins	Poly caprolactone	[32]	

To remove such contaminants from wastewater, a variety of classic and innovative technologies have been used, viz. adsorption, coagulation, precipitation, ion exchange, solvent extraction, membrane filtration, flocculation, and electrolytic and biological processes. Out of these, biopolymers-based adsorption, coagulation, and flocculation are extensively used separation techniques for the removal of heavy toxic metals and compounds, suspended and dissolved particles, and colloids present in industrial wastewater [45]. These are simple and effective wastewater treatment procedures that have a wide range of applications in wastewater treatment [20].

There is an urgent need for the development of technologies that enable the removal of hazardous contaminants from wastewater.

Biosorption is one of the most popular and efficient metal remediation methods. The large number of papers published on the adsorption and remediation of metal ions from aqueous solutions by natural and modified polysaccharides demonstrates a growing interest in biopolymer applications for environmental preservation [12].

In the laboratory, these biopolymers have been successfully tested for pollutant removal from wastewater. Based on the bio-flocculating materials and the wastewater characteristics, these bio-based or microbial flocculants could efficiently lower suspended solids (SS), heavy metals, chemical oxygen demand (COD), total nitrogen content, dye, and turbidity by up to 90% in some situations [35].

Organic polymeric flocculants are currently extensively employed because of their exceptional capability to flocculate effectively at a lower dose [42]. However, it is not preferred due to its non-biodegradability and the dispersion of monomer residues in water, which could pose a health risk. Although synthetic polymers as flocculants have a wide range of applications, their use is contentious because it may have negative environmental and health consequences. The most common hazardous substances, in the case of use of synthetic polymers for wastewater treatment, includes unreacted chemicals such as *epi*-chlorohydrin, dimethylamine, and formaldehyde that are used to produce the monomers, unreacted residual monomers, like acrylamide, ethyleneimine, and reaction by-products of the polymers in water. Acrylamide is a highly toxic substance that causes severe neurotoxicity. According to the study, cationic poly-electrolytes are more hazardous, especially to aquatic animals, as compared to anionic and non-ionic polymers that are generally less toxic. Furthermore, almost all commercially available polymers are manufactured or processed from petroleum-derived basic components that aren't always safe or environmentally friendly. In addition, these are resistant to biodegradation or their degradation is quite slow, and their degraded monomeric products are still hazardous and have carcinogenic effects upon entering into the food chain. As a reason, the demand for environmentally safe biopolymer-based flocculants, generated from natural sources with effective coagulation properties, is increasing [43].

As a result, scientists all over the world are putting effort to develop these natural flocculants that could potentially replace synthetic flocculants. The challenge now is that natural flocculants are required in large doses due to their low flocculating efficacy and limited shelf life. To generate tailor-made grafted flocculants, synthetic polymers are grafted onto the backbone of natural polymers to combine the best features of both [50].

2.1 Natural Bio-flocculants

As the demand for eco-friendly materials in wastewater treatment has increased in recent years, traditional flocculants have been replaced by bio-flocculants as a feasible alternative. Bio-flocculants derived from natural polysaccharides or other natural polymers such as alginate, cellulose, chitosan, gums, mucilage, and tannins, have attracted researchers' [42] interest as they offer a lot of potential in treatment of wastewater from food and fermentation industry, pharmaceutical industry and cosmetic industry.

Bio-flocculants' mode of action of pollutant removal involves destabilisation of colloidal particles by an increase in the ionic strength that results in a decrease in zeta potential and, consequently, a thinner diffuse section of the double electrical layer. Alternatively, these polymers may selectively absorb counterions to neutralise the charge of particles and thus interact with pollutants due to the presence of diverse functional (carboxyl or hydroxyl) groups in their macromolecular structures [18].

2.1.1 Mode of Action for Natural Bio-flocculants

The natural polymer chitosan's depolluting activity depends on its cationic nature, due to reactive functional groups like amino groups and/or hydroxyl groups and a large molecular weight that can lead to charge neutralisation by coagulation and flocculation of pollutants by bridging mechanisms.

According to a study that examined chitosan's coagulation and flocculation potential for dye removal from the solution, it was revealed that protonated amine groups from chitosan electrostatically attract the anionic dye resulting in charges neutralisation, and further, the flocculation was enhanced leading to agglomerates binding with each other and settling by the bridging mechanism [18].

Many factors influence chitosan's activity to form hydrogen bridges or for hydrophobic interactions like the nature of the colloids, its molecular weight and level of deacetylation, pH of the suspension, and its dosage. For other natural polymers that are anionic, for example, cellulose, or tannin, they also require the help of cations to flocculate anionic contaminants from wastewater. Thus, cationic polymers such as chitosan or inorganic metal salts (aluminium or ferric salts) are added for charge neutralisation of negatively charged contaminants before the addition of anionic natural flocculants. After neutralisation of charge, anionic cellulose, sodium alginate or tannin with a negatively charged backbone allowed the polymer extension in solution and created loops and tails to aid bridging of flocs [50].

It's worth noting that most plant-based bio-flocculants, for example, that are anionic or non-ionic can be utilised directly in wastewater treatment without any coagulants' help. One such study investigating the flocculation potential of *Plantago psyllium* mucilage and *Tamarindus indica* mucilage for textile wastewater concluded

polymer bridging as a probable flocculation mechanism. The flocculation process of other plant-based bio-flocculants like Mallow and Tamarind mucilage could not be predicted if the surface charge is not known [18].

2.2 *Grafted Flocculants/Graft Copolymers*

Graft copolymers for wastewater flocculation have been developed in response to the growing market demand for efficient and cost-effective flocculants in wastewater treatment. Grafted copolymers have thus evolved as novel materials with enormous potential for wastewater treatment due to their unique characteristics and higher performance over conventional polymeric flocculants. Natural polysaccharides have been modified to combine their best characteristics with existing synthetic polymers and hence improve the flocculation ability by increasing the percentage of effective constituent and positive electric charge of the flocculants [47]. Polysaccharides, unlike long-chain synthetic polymers, are relatively shear stable and biodegradable. However, because of their poor efficiency, greater concentrations or dosages are required. It is apparent that irrespective of natural or synthetic nature, all polymers have some disadvantages. By grafting synthetic polymers onto the backbone of natural biopolymers, numerous attempts have been made to combine the best features of each. Some examples of grafted flocculants include polyacrylamide grafted-starch, polyacrylamide grafted-hydroxypropyl methylcellulose, polyacrylamide grafted-carboxymethyl guar gum, polymethylmethacrylate grafted -psyllium, and poly (2-hydroxyethyl methacrylate) grafted -agar [47]. The flocculating property of these copolymers has been successfully investigated in kaolin suspension (synthetic wastewater) by the Jar test method suggesting that these flocculants might be used in commercial wastewater treatment. Many more copolymers have been effectively produced by grafting polyacrylamide or polytrimethyl ammonium chloride chains onto natural biopolymers like agar, celluloses, chitosan, gums, sodium alginate, starches, and oatmeal [45]. The flocculating capabilities of these have been tested in a variety of wastewater effluents (e.g., municipal sewage effluent, pulp mill effluents, raw mine wastewater, and textile effluent). The experiments revealed that flocculating efficiency of grafted copolymers in an aqueous solution is dependent on their molecular extensions. Thus, by varying the length and number of grafted polyacrylamide chains, graft copolymers' efficiency can be modulated. It was found that graft copolymers with high molecular weight and branching status are more efficient flocculating agents even at a lower dose. The occurrence of grafted polyacrylamide chains also increased the hydrodynamic volume (i.e., the radius of gyration) of a polymer in solution, improving its flocculation capacity, according to the simple approachability model of flocculation. Studies have also shown that graft copolymers are better in turbidity removal as compared to commercially available flocculants. Grafting alters the structure of natural polysaccharide molecules, making it less appropriate as a substrate for enzymatic breakdown and is reported to be less vulnerable to biodegradation. Furthermore, grafting polysaccharides enhances the inert polyacrylamide

content, making it less susceptible to biological attack and more resistant to biodegradation. Grafting shear degradable polymers onto the rigid polysaccharide backbone also results in systems that are relatively shear stable. Cationic organic flocculants are more effective in removing negatively charged pollutants or particle suspensions such as clay and dye. Consequently, grafted cationic flocculants have been produced by combining a cationic moiety N-(3-Chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) with the guar gum or starch backbone in the presence of sodium hydroxide. These CHPTAC-based cationic flocculants showed better flocculation performance to remove negatively charged particles in suspension as against commercially available flocculants. However, a certain type of wastewaters like textile effluent is more complex and may contain both unwanted cationic and anionic colloidal particles. As a result, amphoteric flocculants containing both cationic and anionic ions were proposed to remove both cationic and anionic pollutants. Chitosan-based amphoteric flocculants have been produced in recent years, and their flocculating properties have been assessed in kaolin suspension, raw river water, and dye-containing solution. In comparison to chitosan alone, amphoteric chitosan copolymer exhibited greater removal potential and formed noticeably more compacted flocs. In a nutshell, grafting is a very efficient method of modulating the characteristics of polysaccharides so that they can be “tailor-made” to meet specific requirements and make highly efficient graft copolymers. However, the absence of commercial production methods remains the major challenge with graft copolymers. The most common ways to make grafted polysaccharides involve the use of chemical-free radical initiators, i.e., the conventional approach, high-energy X-ray and gamma radiations, UV-radiation-based procedures, and microwave-based methods. In the conventional approach, a chemical-free radical initiator such as ceric ammonium nitrate (CAN) is used to generate free radical sites on the backbone polymer, where the graft monomer is added up to form the graft chain. This method of synthesis is not suited for large-scale industrial applications due to its limited reproducibility.

The use of high-energy radiation as the free radical initiators is a better way of graft copolymer production, but this method can damage the polysaccharide backbone by the process of radiolysis. The UV radiation approach requiring the presence of a photosensitiser can also be utilised, but due to the poor penetration of UV radiation, it is only suited for surface grafting. The best approach for graft copolymer synthesis until now is to use microwave radiation to produce free radical sites on the backbone polymer, however, this method has a high input cost. In conclusion, more studies are needed to find an ecologically friendly and economically viable approach for producing high-quality grafted flocculants with outstanding pollutant removal capabilities, and these modified products can be used to treat a variety of industrial effluents [18].

2.2.1 The Mechanism for Grafted Flocculants/Copolymers

Grafted flocculants or copolymers utilise charge neutralisation and polymer bridging as a flocculation mechanism for wastewater treatment. At the start of the flocculation

process, charge neutralisation predominates, resulting in the rapid production of a large number of insoluble complexes. The insoluble compounds then combine and form bigger net-like flocs due to the bridging effect of the flexible polymeric graft chains. Finally, the compacted flocs are generated that settle quickly. Other studies suggested polymer bridging as the dominant flocculation mechanism [1]. The reason that graft copolymers have greater flocculation qualities than linear polymers is related to the polymer bridging mechanism. Polymer chain segments get adsorbed onto the surfaces of distinct particles, bridging and linking all the nearby particles. Due to the longer polymeric chain of grafted flocculants and greater gyration radius, the adsorbed polymers tend to assume a more stretched structure thus interacting with multiple particles [49].

3 Polysaccharide-Based Products for Wastewater Treatment

Polysaccharides are polymers of carbohydrates, in which monosaccharides (for example, cellulose, chitosan, glycogen, and starch) join through glycosidic linkages to form long linear chains [50]. Polysaccharides are hydrolysed to produce monosaccharides or oligosaccharides [11]. These have gained attention as bio-based flocculants in drinking-water and wastewater treatment attributed to their unique properties, including accessibility, biodegradability, and structural characteristics that facilitate functional modifications [23, 42] (Fig. 3).

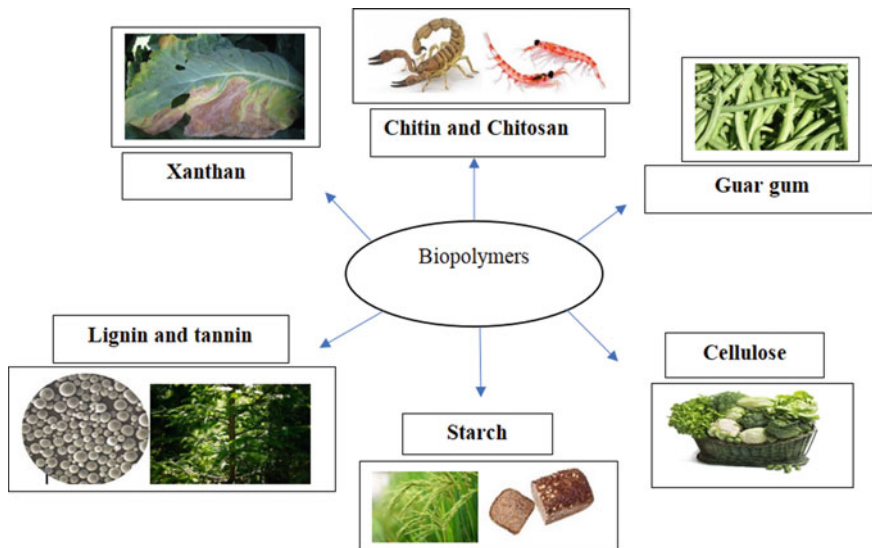


Fig. 3 Polysaccharide-based products for wastewater treatment

3.1 Chitosan

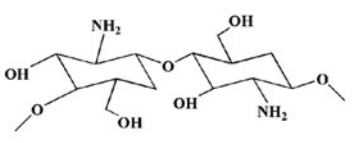




Chitosan is a linear polysaccharide comprising monomeric units of N-glucosamine (deacetylated) and N-acetyl-D glucosamine linked through β -1, 4 glycosidic bonds [5]. The order and distribution of the two monomers along the chain determine their physical, chemical, and biological properties [28]. It is obtained by deacetylation of chitin, a natural biopolymer found in exoskeletons of crustaceans, shellfish, arthropods, fungi cell walls, and insects [32]. Chitin and chitosan, being biodegradable and non-toxic, have diverse applications. As chitosan produces hydrocolloid and causes gelling of water, it can be utilised as food additives, thickening agents, and coating agents in the food industry. In cosmetics, it is used to make skin-care products and creams [5]. Chitosan is also employed in drug delivery systems, for enzymes and microbial cell immobilisation. It can be used as a biocontrol agent for handling plants diseases. It may be used for making porous materials for bioreactors [30].

Since chitosan is a polycationic macromolecule, it can be a promising flocculant as most natural colloids are negatively charged. Chitosan is insoluble in water and organic solvents. But it is soluble in dilute organic acids (like acetic and formic acid) and inorganic acids, due to the protonation of the free amino groups [28]. In acidic solutions ($\text{pH} < 5$), chitosan transforms into a soluble cationic polymer with a high charge density that can electrostatically interact with negatively charged contaminants, such as metal anions, dyes, and organic compounds, present in wastewater. Owing to its adsorption properties, it can also be for the removal of suspended and dissolved solids [28].

Different chitosan-based products such as films, nanofibers, powder, and beads have been generated through various physical modifications [38, 9, 3, 17]. Chitosan-based biocomposites have recently been developed, to overcome chitosan's limitations and provide physical strength and magnetism [8, 19]. Further, scientists have produced chitosan nanofibers with adjustable pore sizes and large specific surface areas [19, 10]. Pure chitosan nanofiber membranes (129 nm diameter) developed by the electrospinning technique could be used for as Vanadium (V) removal from water [25]. Likewise, chitosan-polyvinyl alcohol or zeolite nanofiber composite has been developed by blending and electrospinning technique [9]. Such nanofiber composites are reusable up to five times and are stable at various pH [27].



Chemically modified chitosan derivatives have superior adsorption capacity, mechanical resistance, and chemical stability [32]. Many studies have successfully evaluated its flocculation and coagulation properties for dye removal, organic matter (e.g., lignin and chlorinated compounds), heavy metals, and phenolic compounds removal in textile, pulp and paper mill, and cardboard-mill wastewater [18] (Table 2).

Table 2 Chitins and Chitosans' potential in pollutants' removal

Chitin and Chitosan			
			
Sources	Products	Applications	References
 crab	Chitosan Particles, Aerogels, Composites	Dyes and Metals removal	(Russo <i>et al.</i> , 2021)
	Water-soluble flocculants and Nano sorbents	Organic pollutants/Oil	(Jacob and Gopi, 2021)
	Beads	Drug/emerging pollutants	(Sarode <i>et al.</i> , no date)
 Scorpions	Carboxylated chitosan/Fe ₃ O ₄	Fluoride, nitrate and phosphate removal	(Pandey, 2020)
 Crustaceans	Chitosan solution	Turbidity and TDS removal	(No and Meyers, 2000)
 Locust	Carboxy methyl chitosan-graft-polyacrylamide (CMC-g-PAM)	Dye removal	
	Carboxy methyl chitosan-g-poly(2-methacryloyloxyethyl) trimethyl ammonium chloride	Dye removal	(Chen <i>et al.</i> , 2020)

(continued)

Table 2 (continued)

 fungi	(CMC-g-PDMC)		
	Chitosan grafted copolymer of acrylamide and 3-acrylamide propyl trimethylammonium chloride (CTS-g-PAA)	Dye removal	(Fouda-Mbanga, Prabakaran and Pillay, 2021)
 Starfish	Chitosan-acrylamide-fulvic acid (CAMFA)	Colour removal	(Zubair and Ullah, 2021)
	Amphoteric carboxy methyl chitosan (CMC-CTA)	Turbidity removal	(Maćczak <i>et al.</i> , 2020)
	Carboxylated chitosan-graft-polyacrylamide co-sodium xanthate	Turbidity removal	(Fouda-Mbanga, Prabakaran and Pillay, 2021)
	Carboxylated chitosan-graft-poly (acrylamide-2-acrylamido-2-methylpropane sulfonic acid (CPCTS-g-P(AM-AMPS))	Heavy metal removal	(Pal <i>et al.</i> , 2021)
	Chitosan graft-poly (acrylamide-acryloyloxyethyl) trimethylammonium chloride (CS-g-PAD)	Zinc phosphate removal	(Yue <i>et al.</i> , 2019)

3.2 Gums and Mucilage

Plant-based gums and mucilages have emerged as an environment-friendly green technology for wastewater treatment and have been endorsed as a safer and valuable alternative to existing traditional inorganic coagulants [32]. The common plant species as a source of gums, that have been used to develop flocculants, includes Hibiscus (Okra), *Malva sylvestris* (Mallow), *Plantago psyllium* (Psyllium), *Plantago ovata* (Isabgol), *Tamarindus indica* (Tamarind), and *Trigonella foenum-graecum* (Fenugreek) [51]. Aqueous extraction, alcohol precipitation, and drying are the most common methods for obtaining plant-based flocculants [27].

They have demonstrated promising results for the removal of COD, colour, total suspended solids, and turbidity, in the treatment of landfill leachate, effluents from textile, tannery, and sewage. In terms of treatment efficiency, some plant-based gums showed equivalent efficacy to synthetic flocculants even at low concentrations. Okra gum (0.12 mg/L) and Fenugreek mucilage (0.08 mg/L) were able to remove >85% of suspended particles from sewage wastewater and tannery effluent, which is comparable to synthetic polyacrylamide [27].

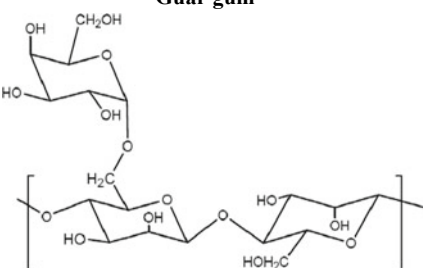

A gum xanthan-psyllium-cl-poly (acrylic acid-co-itaconic acid)-based adsorbent has been successfully tested to remove the dyes such as Auramine O (Aur-O) and Eriochrome black T (EBT) from the aqueous solutions and is also recyclable with less reduction in activity up to six and three cycles, respectively [4]. Likewise, grafted binary psyllium (Psy-g-Poly) was recently produced and evaluated for Hg (II) ion removal from an aqueous solution. Even at a high concentration of Hg (II) ions (100 ppm), the adsorbent showed a great (approx. 96%) adsorption effectiveness [32] (Table 3).

3.3 Cellulose

Cellulose, one of the most abundant natural fibrous polysaccharides, is a linear chain polymer of β -1, 4 linked D-glucopyranose and is obtained mainly from wood sources and cotton [32]. Even though the applications of pure cellulose are very limited, modifying its physical and chemical properties, for example, direct chemical modification of hydroxyl groups of cellulose by various agents, has recently received great attention to improving its industrial applications. The chemically modified cellulose or its derivatives can be obtained either by incorporating chelating or metal binding functional groups directly into the cellulose [39] or alternatively, grafting the monomers to cellulose [51].

Etherification, esterification, oxidation, and halogenation are the most common cellulose functionalisation processes [32]. The chemically modified cellulose shows improved adsorption for heavy metals in aqueous and non-aqueous solution and also exhibits altered properties like hydrophobicity or hydrophilicity, elasticity, microbiological, heat, and mechanical resistance [29, 24]. Cellulosic materials have numerous

Table 3 Gum-based products and their applications for wastewater treatment

Guar gum			
			
Sources	Products	Applications	References
 <u>guar beans</u>	HPTAC-guar (Hydroxyl propyltrimmonium chloride guar gum)	COD Removal, turbidity removal and biological Contaminants removal from municipal wastewater	(Russo <i>et al.</i> , 2021)
	CGG (cationized guar gum)	Bentonite aggregation	(Jacob and Gopi, 2021)

applications ranging from medical, pharmaceutical, cosmetics, energy storage materials to nanocomposites, membranes, and barrier films, as well as electronics, sensors, and supercapacitors [27].

Anionic sodium carboxymethyl-cellulose (CMCNa) produced from date palm rachis, an anionic water-soluble polyelectrolyte that is renewable, non-toxic, and biodegradable, has been explored as an environment-friendly flocculant for turbidity removal in drinking water treatment, together with aluminium sulphate (as a coagulant). Another study tested the flocculating performance of ionised Dicarboxylic acid nano-cellulose (DCC) flocculant (with ferric sulphate as a coagulant) in municipal wastewater. Nanofibrils cellulose (NFC) and cellulose nanocrystals (CNCs) have recently gained significant attention as Nano-sorbents because of their unique features and are examined for wastewater treatment. Although various studies highlighted the efficacy of cellulose-based nanomaterials in the removal of different contaminants, their environmental consequences, as well as their non-toxicity and biodegradability characteristics, still need to be evaluated [29].

3.3.1 Membranes for Water Treatment

Cellulose-based nanofibers (CNF) or cellulose microfibrils have been used for the development of biocomposite membranes with CNF embedded in a polymer matrix (cellulose triacetate, poly-pyrrole, poly-(ether sulfone), poly-(acrylonitrile), poly-(ethylene oxide), poly-(vinyl alcohol), poly-(vinylidene fluoride), and poly-(3-hydroxybutyrate)). These biocomposite-based membranes, created from fibre-reinforced biopolymers, have been tested for distillation, haemodialysis, and filtration [18].

3.3.2 Different Chemical Treatments

Recently, various chemical treatments have been used to modify the surface of cellulose-based nanomaterials to improve their affinity for hydrophobic materials and the removal of organic pollutants.

Microbial cellulose surfaces coated with TiO₂ (MC/TiO₂) have been used to degrade toluene in air at room temperature when exposed to UV light [36]. Likewise, cellulose nanofiber (CNF) aerogels coated with triethoxyl (octyl) silane, by vapour phase deposition method, resulted in the production of reusable hydrophobic materials having a strong affinity to oils and thus improved sorption efficiency for organic solvents. Wang et al. [44] evaluated the Nano-cellulose-based hydrogels that were modified with graphene oxide for sorption of cyclo-hexane and dimethyl-formamide (DMF).

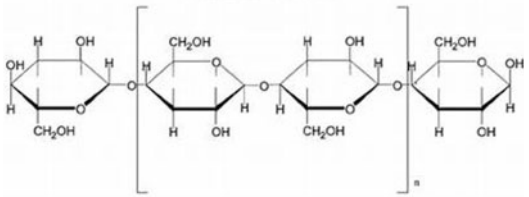



Reusable sponge-like (micro- or Nano-sized) systems have been created, by thermal crosslinking of (2, 2, 6, 6-Tetra-methylpiperidin-1-oxyl) (TEMPO)-oxidised cellulose nanofibers (TOCNF), citric acid, and branched poly-ethylene-imine (bPEI), with improved adsorbent efficacy for diverse dyes, for example, Brilliant Blue R, Cibacron Brilliant Yellow, and Naphthol Blue Black [51].

Crosslinking the self-assembled TO-CNF with Tri-methylolpropane-tris-(2-methyl-1-aziridine) propionate (TMPTAP) and poly-ethylene-imine (PEI) had efficient Cu (II) adsorption capability [18]. A study demonstrated that nano-cellulose-based aerogels/fibres with a very thin layer of TiO₂ nanoparticles (low-energy surface layer) had improved with oleophilic and hydrophobic properties and thus can be used for oil and organic solvent removal from water [12].

Another study evaluated and compared the dye and heavy metal adsorption abilities of lignocellulose-based materials, before and after physical and chemical treatment and concluded that altering their physical and chemical properties improves their qualities and expands their industrial applications [51]. Anionic sodium carboxymethyl cellulose (CMC Na), made from date palm rachis waste, was investigated as an environment-friendly flocculant for removing turbidity in drinking water treatment, together with aluminium sulphate as a coagulant [27].

Another study created an ionised dicarboxylic acid nano-cellulose (DCC) flocculant and tested its flocculating potential in municipal wastewater using ferric sulphate as a coagulant [45] (Table 4).

Table 4 Cellulose-based products and their applications in wastewater treatment

Cellulose			
Cellulose Structure			
			
Sources	Products	Applications	References
 Fibre which vegetable	Anionic cellulose	Textile effluent treatment	(Olivera <i>et al.</i> , 2016)
	Cationic cellulose	Colour removal	(Fouda-Mbanga, Prabakaran and Pillay, 2021)
 Sugarcane	Quaternized-cellulose (QC)	Anionic dyes removal	(Yue <i>et al.</i> , 2019)
	Aerogels, fibres, membranes	Organic pollutants/oil, heavy metals Removal	(Fouda-Mbanga, Prabakaran and Pillay, 2021)
 Cotton	Hydroxy-propyl methyl cellulose grafted with polyacrylamide (HPMC-g-PAM)	Kaolin and iron-ore suspension Clarification	(Asif <i>et al.</i> , 2021)
	Sodium- carboxy methyl cellulose (CMCNa) and Carboxymethyl cellulose-g-polyacrylamide (CMC-g-PA)	Turbidity removal from drinking water and Clarification of Kaolin suspension, respectively	(Zubair and Ullah, 2021)

(continued)

Table 4 (continued)

	Nano-sorbents and Nanostructured materials	Dye and Heavy metals Removal	(Maćczak <i>et al.</i> , 2020)
	Dicarboxylic acid nanocellulose (DCC)	Turbidity removal and Municipal wastewater treatment	(Pandey, 2020)
	Cationic cellulose nanofibers (CCNF)	Pulp slurry flocculation	(Jacob and Gopi, 2021)
	Poly acryloyloxy ethyl trimethyl ammonium chloride-g-cellulose nanocrystal (PAETMAC-g-CNC)	Colour Removal.	(Olivera <i>et al.</i> , 2016)
	3 anionic sulfonated nanocellulose (ADAC)	Turbidity and COD removal	(Maji and Maiti, 2021)
	Grafted microcrystalline cellulose MCC (pAA-co-pDMC)	Turbidity and Colour removal	(Zhao <i>et al.</i> , 2020)

4 Other Polysaccharides

Other polysaccharides-based polymers like alginate, lignin, and starch have also been tested for wastewater treatment. For example, grafted copolymer of starch with acrylamide and dimethyl-diallyl ammonium chloride was reported for the wastewater treatment from textile effluent. In comparison to a traditional coagulation-flocculation procedure, this composite coagulant reduced the requirement of chemical dose by more than 50% [2, 11].

4.1 Starch

Starch is a key energy source that is made up of grain products in the proportions of 60% to 75% by weight [49]. It consumes between 70 and 80 per cent of the calories produced by the human body or living thing [27]. Typically, starch-based products are added to alter the physical qualities of food, and they have a variety of applications including thickening agent, adhesive, and moisture retention material [11, 49] (Table 5).

4.2 Tannin

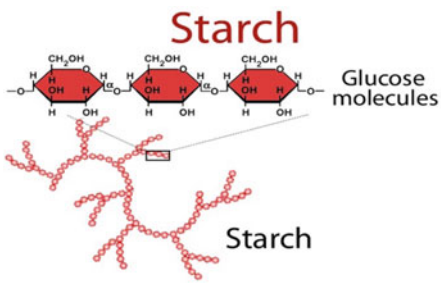



Tannins are secondary metabolites and anionic polymers found in fruits, leaves, and bark and are biodegradable in nature [32]. Their flocculating ability has been studied for removing various pollutants found in drinking water as well as wastewater, for example, suspended, colloidal materials, dyes, inks, and pigments. During the process, first a coagulant such as aluminium sulphate neutralize the negative charge making colloidal particles unstable, while anionic tannin acts as a flocculant to link the destabilised aggregates together to create flocs large enough to sediment. The study proved that combining aluminium sulphate (used as a coagulant) with tannin (used as a flocculant) considerably decreased the amount of coagulant required for treatment. Modified tannin (Tan flocculant) overcomes the need for coagulant for the treatment and has recently been evaluated for heavy metals removal with high efficiency from polluted surface water and municipal wastewater. Tan flocculant is manufactured from *Acacia Mearnsii* bark that has undergone physio-chemical modifications that impart cationic characteristic. The chemical change includes the addition of a range of hydrocolloid gums and soluble salts containing substituted amino sites in the structure. Owing to its cationic characteristic, direct flocculation was achieved without the need for any coagulant or pH correction [45, 48].

A novel adsorbent poly (tannin-hexa-methylene-diamine) (PTHAM), produced by the one-pot green synthesis method, was evaluated for Cr (VI) exclusion from water by changing the molar ratio of tannin and hexa-methylene-diamine. Further, by using tannin grafted on cellulose (TM) microfibers, the cationic dye was successfully removed from the aqueous solution recently [32] (Table 6).

4.3 Alginates

Alginate is a heteropolysaccharide made up of 1 → 4-linked-β-d-mannuronic (MA) and 1 → 4-linked α-guluronic acid monomers (GA) [16]. Stanford was the first to isolate it in 1881. In nature, alginate is found as salts of calcium, magnesium, and sodium with alginic acid and is present in a variety of species of Phaeophyceae,

Table 5 Starch-based products and their application in wastewater treatment

Starch			
			
Sources	Products	Applications	References
 <p>Sushi rice</p>  <p>Raw oats</p>  <p>Pumpernickel bread</p>	Cationic starch	Turbidity removal from kaolin suspension, bentonite clay and natural clay	(Russo <i>et al.</i> , 2021).
	Dispersible-cationic starch (DCS)	Clarification of Kaolin suspensions	(Nasrollahzadeh <i>et al.</i> , 2021)
	(2-hydroxypropyl) trimethyl-ammonium chloride etherified carboxy-methyl starch (CMS-CTA)	Clarification of kaolin and hematite suspension	(Schmidt, Kowalczyk and Zielinska, 2021)
	Polyacrylamide grafted starch (St-g-PAM)	Clarification of kaolin suspension	(Maćczak <i>et al.</i> , 2020)
	Hydroxyethyl starch-grafted poly (N, N dimethyl-acrylamide-co-acrylamide) HES-g-poly-(DMA-co-AM)	Metal ions and dye removal	(Zhao <i>et al.</i> , 2020)

i.e., brown seaweed. *A. nodosum*, *L. hyperborean*, *M. pyrifera*, and *S. japonica* are used to produce commercial alginates. Alginates of bacterial origins have also been documented; however, this type of alginate is not yet commercially available. Alginate extraction is a relatively simple procedure that has been well documented in the literature [6, 18, 42].

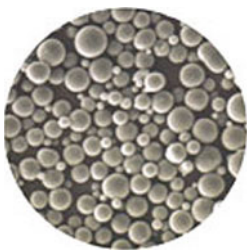
These have robust metal ion chelating properties owing to the occurrence of several functional groups like hydroxyl ($-\text{OH}$), carboxylic ($-\text{COOH}$), and oxo/carbonyl

Table 6 Applications of Lignin- and Tannin-based polymers for wastewater treatments. *Source [37]*

Lignin and tannin			
<p style="text-align: center;">Lignin $\xrightarrow[-H_2O]{H^+}$ $\xrightarrow{HSO_3^-}$ Benzylicsulfonic Acid</p>			
Sources	Products	Applications	References
<p style="text-align: center;">lignin</p>	Kraft lignin copolymer (KLD)	Turbidity removal	(Pandey, 2020)
	Sulfo-methylated softwood kraft lignin (OSKL)	Cationic dye removal	(Lee <i>et al.</i> , 2014)
	Tannin	Turbidity removal	(Zhang <i>et al.</i> , 2017)
	Tanfloc (plant-derived modified tannin)	Heavy metal removal	(Wang <i>et al.</i> , 2021)
	A-TN, Q-TN (modified larch tannin and its quaternized derivative)	Algal water treatment	(Jacob and Gopi, 2021)

(C=O) groups. Sodium alginate is a linear water-soluble anionic polymer (500,000 average molecular weight) that has been investigated for its flocculating efficiency for textile wastewater treatment and synthetic colour removal, with aluminium sulphate used as a coagulant [27]. The findings of the experiments showed that it has great flocculating potential, and treatment leads to colour removal (>90%) and COD reduction (80%) [18]. Because of its benign nature, durability, biodegradability, and water permeability, alginate is widely used in wastewater remediation for pollutant adsorption [13, 16] (Table 7).

Table 7 Metal ion sorption properties of alginate-based products

Source	Alginate-based products	Adsorbent Metals	References
	Carboxylated alginic acid	Cu (II), Pb (II)	(Nasrollahzadeh <i>et al.</i> , 2021)
	Alginate beads	Cu (II), Cd (II), Pb (II)	(Fertah <i>et al.</i> , 2017)
	Alginate capsules, Alginate coated gel	Pb (II)	(Shaikh <i>et al.</i> , 2021)
	Hybrid beads of sodium alginate with chitosan microspheres	Pb (II), Cr (VI)	(Russo <i>et al.</i> , 2021)

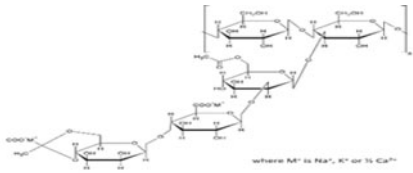

4.4 Xanthan

Xanthan gum, a complex copolymer produced by a bacterium, i.e., *Xanthomonas campestris*, was one of the first commercially effective bacterial polysaccharides to be developed through fermentation [21]. Xanthan is a polymer with five distinct sugar groups as “repeat units”. It’s widely utilised in both the food and non-food industries [14].

Xanthan and other natural gums have been suggested as a safer substitute to industrial flocculants in wastewater treatment [21]. *Xanthomonas campestris* ferments carbohydrates to produce hydrocolloids, which includes glucose, mannose, and glucuronic acid, as well as partially esterified acetic and pyruvic acids [30, 51].

Xanthated chitosan has been investigated to reduce the Cu (II) ions in kaolin suspensions. Further, a free radical-mediated grafting process in an inert environment was used for the production of polyacrylamide grafted xanthan gum/silica (XG-g-PAM/SiO₂) [21] that has been explored to reduce the turbidity in kaolin- and iron ore-suspensions [27]. In a study, novel hybrid nanocomposites were prepared, by introducing silica nanoparticles into the graft copolymer by hydrolysis and condensation of Tetra-ethyl-ortho-silicate (TEOS), and its flocculation properties were successfully tested for turbidity removal from effluent in a dose-dependent manner [23] (Table 8).

Table 8 Xanthan-based products and its application in wastewater treatment

Xanthan			
			
Source	Products	Applications	References
	Polyacrylamide grafted xanthan gum/silica (XG-g-PAM/SiO ₂)	Turbidity removal	(Russo <i>et al.</i> , 2021)
	Tetra ethyl ortho silicate (TEOS).	Iron metal removal	(Maji and Maiti, 2021)
	Xanthated chitosan	Cu(II) ions removal	(Pal <i>et al.</i> , 2016)

4.5 Pullulan

Some studies have evaluated the pesticide-flocculation properties of pullulan or its derivatives in wastewater. The pullulan can be modified to contain pendant tertiary amine or quaternary ammonium salts. Ghimici and co-workers based on UV/Visible spectroscopy analysis revealed strong interaction of pesticide particles with poly-cations resulting in efficient, about 80–98%, pollutant removal. Moreover, zeta potential measurements verified charge neutralisation as the main flocculation mechanism but chelation and hydrogen bonding can also be the probable flocculation mechanism.

5 Advantages and Limitations of Using Polysaccharide-Based Products for Metal Ion Adsorption

5.1 Advantages of Natural-/Biopolymers

In comparison to typically used sorbents, such as activated carbon and synthetic ion-exchange resins, for removing metal ions from aqueous solutions, polysaccharide biopolymers have many advantages:

- These are economic and are derived from natural raw resources as compared to the majority of commercially available petroleum-based polymers and ion-exchange resins that are non-safe and detrimental to the environment. Because of this reason, naturally derived low-cost alternatives are gaining popularity over synthetic polymers.
- Polysaccharide bio-sorbents are incredibly cost-effective to utilise since they are easy to prepare quality crosslinked materials from low-cost reagents and also have minimal operational and maintenance costs. While the activated carbon and ion-exchange resins are very costly, increasing the quality increases the input cost [46].
- Because of the versatile nature of the materials in terms of variable structure and properties, bio-sorbents can have multifunctional applications, including the use as insoluble beads, gels, films, membranes, and filters.
- Polysaccharide-based sorbents have a high capacity, high rate of adsorption, and thus are very efficient at removing pollutants at various concentrations. They can also be modified for removing selective pollutants present in solution either at very low or high concentrations [2, 46].
- The modification of functional groups of polysaccharide-based biopolymers can enhance their chelating properties for a large number of contaminants such as dyes, aromatic compounds, and several metal ions.
- The amphiphilic property of crosslinked biopolymers like cyclo-dextrin polymers makes them attractive since they are sufficiently hydrophilic to swell in water, allowing the adsorbate to diffuse quickly, while still possessing extremely hydrophobic sites that easily trap nonpolar contaminants. Activated carbons on the other hand have a poor adsorbing capacity of certain hydrophilic compounds and metal ions [2].

5.2 *Limitations of Natural Adsorbents*

The absence of efficient extraction and purification techniques is the primary barrier to the development of these polysaccharides. The drawbacks to employing polysaccharides in wastewater treatment can be summed up as follows:

- The adsorption qualities of natural polymers are determined by the raw materials used. The adsorption ability of chitin- and chitosan-based products is affected by the polysaccharide's origin, degree of acetylation and deacetylation, molecular weight, solution characteristics, water affinity, and amino group concentration. These variables influence the polysaccharide's swelling and diffusion properties, as well as its characteristics. These difficulties, along with chemical heterogeneity, may explain why scaling up polysaccharide-based products from the laboratory to the industrial scale is problematic.
- Any polysaccharide system must account for the extreme variability of industrial and municipal wastewaters in its design. Each sort of contaminant could



require a different polysaccharide. Each polysaccharide appears to have a unique application in wastewater treatment, as well as inherent benefits and drawbacks. Heavy metal ions have a strong affinity for chitosan-based compounds. The ability of cyclodextrin sorbents to form inclusion complexes with organic molecules, particularly aromatics, is exceptional, but their metal affinity is very weak [46].

- The type of material chosen has a significant impact on performance. The degree of chemical activation and modification determines the adsorption characteristics. The ideal approach for accomplishing selective extraction of chitosan is to utilise a metal-specific ligand but finding a specific ligand for each metal ion has proven impossible.
- Adsorption efficiency is determined by physio-chemical features of sorbents such as porosity and specific surface area. Another issue with insoluble polysaccharide-based materials is that they have poor physio-chemical properties, particularly in terms of porosity. In general, polysaccharides are nonporous and their derivatives have a low specific surface area. Dried pectin compounds, such as sugar beet pulp, have a low specific surface area of about 5 m²/g, but their hydration and water retention ability allow them to achieve a specific surface area of about 300 m²/g. Likewise, chitosan also has a low specific area, which ranges from 2 to 30 m²/g. The specific surface area of glutaraldehyde-crosslinked chitosan beads, epichlorohydrin-cyclodextrin gels, and epichlorohydrin starch beads is 60, 213 and 350 m²/g, while most commercial activated carbons, on the other hand, have a high specific surface area between 800 and 2000 m²/g.
- The performance of the system is determined by the parameters of the wastewater. The complexation of metal ions is highly influenced by pH. The pH of the wastewater plays a significant role in the speciation of metallic ions. Furthermore, under strongly acidic conditions, the chitosan beads' amine groups easily create protonated groups, which cause metal ions to repel each other electrostatically. Protons and metal ions compete for adsorption sites because of protonation.

6 Protein-Derived Materials for Wastewater Treatment

Just like others, protein-based products because of their distinctive properties, such as natural abundance, biodegradability, non-ecotoxicity, and ease of modification due to the existence of many functional groups, have got dramatic attention over the last two decades. Proteins are intriguing options for wastewater treatment because of their unique features. Polymeric proteins like albumin, gelatine, keratin, soy, and silk proteins have been explored for industrial wastewater treatment [51] (Table 9).

Table 9 Protein-derived materials for wastewater treatment

Sources	Products	Applications	References
	Silk proteins	Industrial wastewater treatment	(Russo <i>et al.</i> , 2021)
	albumin		(Martins <i>et al.</i> , 2008)
	keratin		(Zubair and Ullah, 2021)
	Soybean derived proteins		(Jacob and Gopi, 2021)

7 Challenges

Although biopolymers-based flocculants showed notable potential in wastewater treatment, there are still many challenges that need to be overcome. Natural polymers have a lower shelf life than synthetic polymers because their active components deteriorate over time and must be properly regulated [26]. Furthermore, due to their biodegradability, the flocs tend to become less stable and lose strength over time. The majority of natural biopolymers comprise hydrolysable groups alongside the main chain making them susceptible to biodegradation via hydrolysis. Furthermore, several anionic bio-flocculants such as alginate, cellulose, and tannin are efficient only to a certain extent and can only assist the coagulation process. Cationic coagulant is necessary for the neutralisation of charge before bio-flocculant can bridge the microflocs together in the coagulation-flocculation process, and a high dose is required for efficient flocculation. To solve all of these difficulties, a new generation of smart biopolymer flocculants has been produced by optimally grafting synthetic polymeric branches onto pure polysaccharide backbones [18]. Research focusing on the development and characterisation of nano-bio-flocculants with a longer shelf life is being carried out recently. The areas of improvement include selection and identification of new raw materials, the simplification and improvement of extraction methods, improving functional properties and identifying new modifying agents, and industrial-scale-up of this technology.

8 Summary and Conclusion

Natural (bio-)polymers, particularly cellulose, chitosan, and proteins-based polymers, offer remarkable adsorption capacities for wastewater treatment, as well as are cheap, sustainable, and eco-friendly [43]. These properties make biopolymer-based materials a preferred alternative to currently available commercial adsorbing materials. However, large industrial-scale application of biopolymers for removal of organic dyes and heavy metals from fresh water and wastewater is still limited due to high cost, and incapability to remove multiple contaminants simultaneously. In addition, other factors such as the recovery of biopolymers, and the separation of pollutants like heavy metals from the adsorbing material after the adsorption process are critical to outcompete with prevailing adsorbents for commercial wastewater treatment [26].

Irrespective of the disadvantages, biopolymer-based products have a bright future in industrial wastewater remediation. In comparison to their competitors for wastewater purification, biopolymer-based materials offer greater removal efficiency with low input cost, and thus are predicted to see a rise in demand [1]. The development of novel biopolymers with high performance and low environmental impact opens new avenues for researchers and provides them with a variety of chances to better understand and address water pollution challenges. In the coming years, improvements in biopolymer-based products at the commercial scale will provide sustainable and renewable materials for wastewater remediation [32]. Existing technologies are currently incapable of extracting all microbial polysaccharides. The greatest impediment to the marketing of novel polysaccharides is the identification of new or better qualities than those found in existing products. The second impediment to improving original structures is the expense of production and development, which could be a limiting factor once again [14].

Due to their low cost and environmental friendliness, many biopolymers are now utilised in different industries and will be used more in the future. Blending and grafting are two strategies that have been developed to improve the characteristics of biopolymers [43]. Biopolymers are used to make a variety of composites and nanocomposites. Biopolymers' applications include the areas such as bio-medical, tissue engineering, food and packaging industry and automotive industry [20]. Therefore, biopolymers will play an important role in the daily needs of human life in the future.

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Bioplastics from Biomass



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Abstract Fossil-based materials have many positive characteristics that enable numerous hypostasis of the existing lifestyle and the international economy. However, these are imagined as initiator of solid waste and pollution, with a huge negative effect on the environment. Moreover, petroleum-based materials *are* not sustainable, the world being close to using up all non-renewable fossil-based resources. Because of these negative effects on the environment and climate change, the progress of biodegradable biopolymers based on renewable sources has become imperative. This chapter summarizes the biodegradable bioplastics derived from biomass, paying particular attention to bacterial nanocellulose, polyhydroxyalkanoates, and polylactic acid as sustainable food/beverage packaging materials. The use of these biopolymers will find an answer to pollution induced by the petroleum-based polymers and impart a route to a circular economy.

Keywords Bacterial cellulose · Biodegradable · Biomass · Bionanomaterials · Eco-friendly · Packaging · Polyhydroxyalkanoates · Polylactic acid · Renewable · Sustainable

1 Introduction

Petroleum-based materials are a part of modern lifestyle worldwide, being used in numerous applications, such as industrial area (e.g., packaging industry, electronics), commercial, and municipal field, due to their characteristics (relatively cheap; easy to process; high clarity; chemical stability; flexible structures or rigid structures; adequate gas, water vapor, and flavor barrier; impact resistance; mechanical and optical properties), the best part of them being used in the packaging applications [19, 35, 46, 51, 116, 134–140, 137, 138, 144, 149]. Although polymer materials used in the packaging applications possess many benefits, unfortunately they cause waste and pollution, having an extremely negative influence on the environment (where

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these remain for a long period, as well as on public health and economy. The use of petroleum-based materials is increasing; by the year 2050, the petroleum-based material production is expected to have tripled, resulting into huge impact on the environment, the economy, and human health [54, 79, 122, 139, 149, 165]. In the modern world, 25% of the world's actual petroleum production is used only to obtain synthetic polymers, and if this tendency persists, by 2050, 12 billion metric tons of plastic waste will appear in landfills [139, 149]. Moreover, the world is nearly to using up all of its non-renewable petroleum-based resources, which cost the nature millions of years to produce [70]. With the negative influence of fossil-based materials on the environment and climate change, the use of renewable resources has become urgency. This has led to the development of sustainable bio-based materials that possess eco-friendly characteristics. Besides the positive aspects include the use of renewable sources, lower energy consumption during manufacturing, low carbon footprint, chemical recyclability, and biodegradability having biotic/abiotic disintegration as end-of-life [14, 17, 34, 66, 75, 87, 101, 105, 116, 117, 122, 139, 148, 159]. The bioplastic materials can be produced from biomass (renewable sources) and fossil carbon sources (non-renewable) [54, 55, 135, 137, 139, 140, 157, 166]. The bioplastic materials obtained from biomass (bio-based) are biodegradable (e.g., polyssacharide-based and protein-based, polyhydroxyalkanoates—PHAs, polylactic acid—PLA) and non-biodegradable (bio-polyethylene, bio-polyethylene terephthalate, bio-polypropylene, polyol-polyurethane, highly resistant to biological degradation) [43, 48, 87, 98, 139]. The bio-based biodegradable materials can be classified as follows:

- (i) Bio-based biopolymers directly obtained from natural resources (polyssacharide-based and protein-based) and directly synthesized from a broad range of biological systems used as a carbon source by microorganisms (e.g., PHAs).
- (ii) Bio-based biopolymers indirectly synthesized, such as PLA [93].

This chapter focuses on the bacterial nanocellulose, polyhydroxyalkanoates, and polylactic acid as natural-sourced materials with biotic/abiotic disintegration or composting as end-of-life, which have the potential to reduce the petroleum-based materials consumption and to produce a sustainable food/beverage packing field thanks to their eco-friendly characteristics.

2 Natural-Sourced Biopolymers

The natural biopolymers are found in large quantities in nature, such as algae (agar, alginates, carrageenans, galactans), plants (nanocellulose, hemicellulose, glucomannan, gums, pectin, starch), bacteria (nanocellulose, dextran, gellan, levan, polygalactosamine, xanthan), fungi (chitin/chitosan, elsinan, pullulan, yeast glucans), and animals (chitin/chitosan, glycosaminoglycans, hyaluronic acid, keratin) and are

used in all areas of human activities (biomedical, food/beverage industry, packaging, pharmaceutical) [5, 6, 100, 109, 120, 127, 128, 125, 151, 150], Sharma and Kumar, 2019). The most important natural biopolymers refer to polysaccharide-based and protein-based biopolymers, and polyhydroxyalkanoates [150, 151]. In this subsection, emphasis will be laid only on bacterial nanocellulose biopolymer, which can be applied for packaging purposes of various types of food/beverage.

2.1 Bacterial Nanocellulose (BNC)

There are three types of nanocellulose, namely bacterial nanocellulose (BNC), cellulose nanocrystalline, and cellulose nanofibers [99, 135–138, 140]. BNC (also known as bacterial cellulose, biocellulose, microbial cellulose) is a nano-scale form of nanocellulose, being biotechnologically generated by some bacteria, such as *Alcaligenes*, *Escherichia*, *Gluconacetobacter*, *Komagataeibacter* (formerly *Acetobacter*), *Rhizobium*, *Pseudomonas*, *Salmonella*, and *Xanthococcus* which combines the properties of cellulose with the features of nanomaterials. Of these, the genus *Komagataeibacter* (*Komagataeibacter xylinus*, *Komagataeibacter hanseii*, *Komagataeibacter rhaeticus*) is the most common producer of BNC [8, 41, 60]. *Gluconacetobacter* has also demonstrated high BNC productivities [153]. Succinctly, the biosynthesis of BNC initiates with the transport of the glucose (as carbon source) into bacterial cells, where the cellulose precursor uridine diphosphoglucose is formed. Then, glucose is polymerized to β -1,4-glucan linear sequence from uridine diphosphoglucose by the enzyme cellulose synthase. Finally, the cellulose chains that are extracellularly secreted through pores in the cell membranes are crystallized to sub-fibrils, which are further assembled into nanoribbons of 20–60 nm (extremely reduced diameter when compared with plant cellulose fibers) in width well-organized in a highly pure 3D nanofiber network of ribbon-shaped nano- and microfibrils with high degrees of crystallinity, mechanical strength, and water-holding function [3, 8, 9, 28, 30, 61, 90, 118, 137, 138, 151, 154].

2.1.1 Applicability of BNC in Food/Beverage Packaging

BNC ultra-fine structure has remarkable, unique properties, such as biodegradability; renewability; green processing; ability to be shaped to produce tubes, spheres, or membranes during the fermentation period, according to the application demands; high chemical purity (without hemicelluloses, pectin, and lignin), good mechanical properties; good flexibility; great surface area; inertness and non-toxicity; strong hydrophilicity; less energy for purification; and low production costs [8, 9, 30, 41, 133, 135, 140, 142, 151, 154, 156]. In addition, it is characterized by a high crystallinity that contributes to its (i) high thermal stability, an important characteristic when thermal sterilization is required, and (ii) excellent mechanical characteristics [8]. The high surface area, rich in hydroxyl groups of BNC nano-fibrils,

leads to numerous interactions among hydroxyl groups and low-molecular-weight compounds, metal nanoparticles, metal oxides, and polymers [8, 20, 29, 53, 59, 121, 129, 142]. These are interesting features that makes BNC a significant matrix or nanofillers for functionalized nanomaterials for application in many different domains (Fig. 1). Some examples includes acoustics (membrane speaker), cosmetics (carrier of active ingredients or as a structuring agent of cosmetic formulations), environmental protection (absorption of oil pollution, sewage treatment, toxins ultrafiltration water), industrial (food/beverage; packaging: films, nanocomposites; paper: durable banknotes, repairing old books, paper with special properties; textiles: materials for the production of tents and camping equipment, materials with highly absorbent), medical devices, bioprocessing, and pharmaceutical applications, among many other examples [3, 16, 21, 52, 68, 69, 95, 104, 108, 133, 134, 154, 155, 158, 162, 164], Azeredo (2019).

Packaging is a principal part in the food/beverage area, significantly enhancing preservation, handling, transport, and storage, aiming to guard foods and beverages from any biological and physico-chemical contaminants and also to prevent components within the food/beverage from leaking into environment [46, 51, 54,

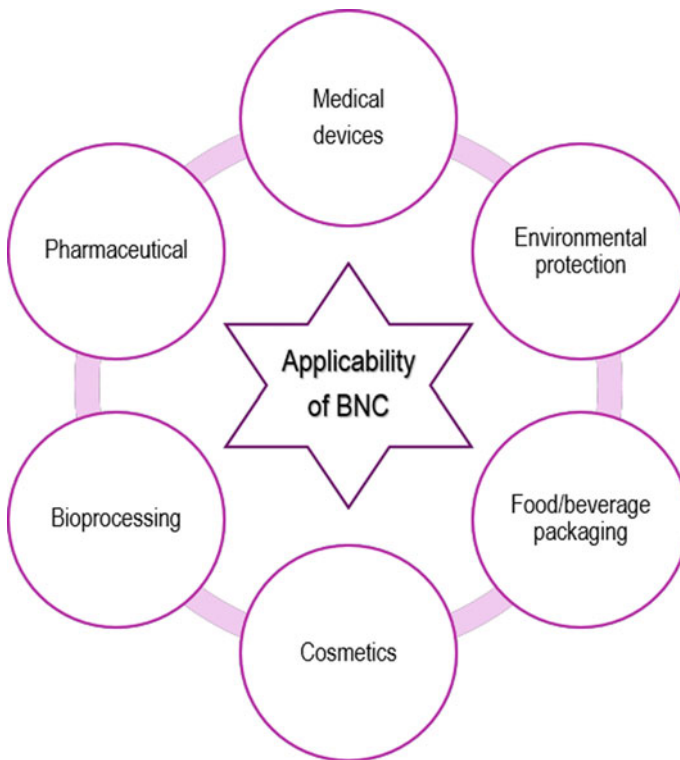


Fig. 1 Areas of BNC applicability

Table 1 Illustrative examples of BNC applications in food/beverage packaging

Engineered BNC nanomaterials	Applications	References
BNC/Methyl red	Intelligent food packaging	[67]
BNC/Lactoferrin	Active food packaging	[94]
BNC/Silver Nanoparticles/Chitosan	Active food packaging	[120]
BNC/Zinc oxide Nanoparticles/Propolis extract	Active food packaging	[82]
BNC/PSBMA (polysulfobetaine methacrylate)	Active and intelligent food packaging	[158]
BNC/ [P(3HB)]/Clove essential oil	Antimicrobial food packaging	[7]
BNC/Silver Nanoparticles/Alginate-molybdenum trioxide nanoparticles	Intelligent food packaging	[143]
BNC/Silver nanoparticles	Antimicrobial food packaging	[162]

132, 137, 138, 163]. Moreover, packaging has a number of other significant roles, such as keeping the color, aroma, flavor, and freshness, as well as gases impermeability (especially in the case of carbonated beverage; improving the traceability and food/beverage security; extending the shelf life of foods and beverages by stopping gas intrusion; and also being user-friendly and eco-friendly [46, 51, 137, 138, 136–139]. It is recognized that the best part of materials used in the foods packaging applications are fossil-based materials, and owing to their characteristics like better clarity; flexible structures (bags and wrappings), or rigid structures (bottles, caps, containers, lids, trays, etc.); adequate gas, water vapor, and flavor barrier; impact resistance; good mechanical and optical properties) [19, 116, 136, 138, 139]. The environmental impact of non-biodegradable petroleum-based materials is an ever-growing global concern. There are solutions to replace those materials with bio-based biodegradable materials, such as BNC. BNC is a promising candidate to replace non-biodegradable fossil-sourced polymers commonly used in foods and beverages packaging [8, 67, 94, 120]. Some illustrative examples of bacterial nanocellulose applications in foods and beverages packing are included in Table 1.

2.2 Polyhydroxyalkanoates (PHAs)

PHAs are bio-synthesized (directly obtained from a broad range of biological systems used as a carbon source by microorganisms) and bio-based (directly obtained from renewable resources) biopolymers, being long-term sustainable alternatives, due to their similar performance to conventional fossil-sourced materials [22, 58, 76, 83, 110, 137]. PHAs are directly synthesized by a range of bacteria and extremophilic archaea (acidophiles, alkalophiles, halophiles, methanotrophs, psychrophiles, thermophiles, xerophiles, and gaseous substrate utilizers from renewable resources as

water-insoluble inclusions within the microbial cells that reveal different composition according to microbial and culture strains [65, 76, 80, 110, 112, 137, 145, 147]. PHAs are generated when the microorganisms are grown in special fermentation conditions such as nutrient-limiting amounts of macrocomponents and microcomponents (magnesium ions, sulfate ions, and other trace elements), and excess carbon sources [48, 102, 145]. Succinctly, some bacteria and extremophilic archaea, when they are exposed to an environmental stress (e.g., depletion of essential nutrients), can convert the carbon sources in PHA units, which are further polymerized into PHA granules through a biosynthetic pathway and stored within the cells [48, 84]. The most prominent polymerizates in PHA systems are poly(3-hydroxybutyrate [P(3HB)]) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [P(3HB-3HV)]. [P(3HB)] is an apolar and optically active biodegradable natural biopolymer, which has been drawing considerable amounts of attentiveness, possessing properties comparable to many petroleum-based polymers [22, 46, 58, 63, 119, 137]. The embedding of hydroxyvalerate into [P(3HB)] polymer results in a [P(3HB-3HV)] polymer, having high flexibility, lower melting temperature, and lower molecular weight than [P(3HB)], being potentially more usable in packaging [1, 46, 137]. [P(3HB-3HV)] is 100% biodegradable semicrystalline polyester, resistant to UV-light and water [11, 78, 168] Resch et al. (2019). However, the water barrier property of [P(3HB-3HV)] is smaller than that of [P(3HB)] [63, 137].

2.2.1 Applicability of PHAs in Food/Beverage Packaging

PHAs are highly tunable and versatile and can be used in various domains (Fig. 2), such as agriculture (biodegradable delivers for insecticide and herbicides; fertilizers and soil conditioners), biotechnology (PHA-based microcapsules), hygiene products (diapers, razors, utensils), packaging, medical (3D printing implants for human, nano-vaccines), and pharmaceutical applications (biodegradable delivers for the long-term dosage drugs, hormones, and so on) [18, 49, 102, 145, 147].

PHAs are high hydro-biodegradable materials, which can completely undergo disintegration into water, CO₂, methane, inorganic compounds, or biomass in various natural environments (landfill, soil, freshwater, seawater) and industrial composting facilities [14, 36, 50, 62, 87, 92, 106, 139, 160, 161]. PHAs can offer an encouraging alternative for a sustainable food packaging industry, exhibiting special characteristics, such as good chemical and mechanical properties, considerable hydrophobicity in comparison to other natural-sourced biopolymers (polyssacharides-based and protein-based), biodegradability, recyclability, compostability, and renewability, showing promise in the concurrence with petroleum-based polymers [10, 50, 54, 62, 76, 110, 116, 137, 139, 159]. However, PHAs still possess several limits (inferior thermal and mechanical stability, poorer moisture and gas barrier, and higher value for flavor permeability than petroleum-based materials [2, 33, 137, 138, 141]). To enhance the PHAs performance, addition of nanoparticles (e.g., nanocellulose, nanoclays, nanosilver, or metal oxides in nanoforms) is considered an efficient strategy [79,

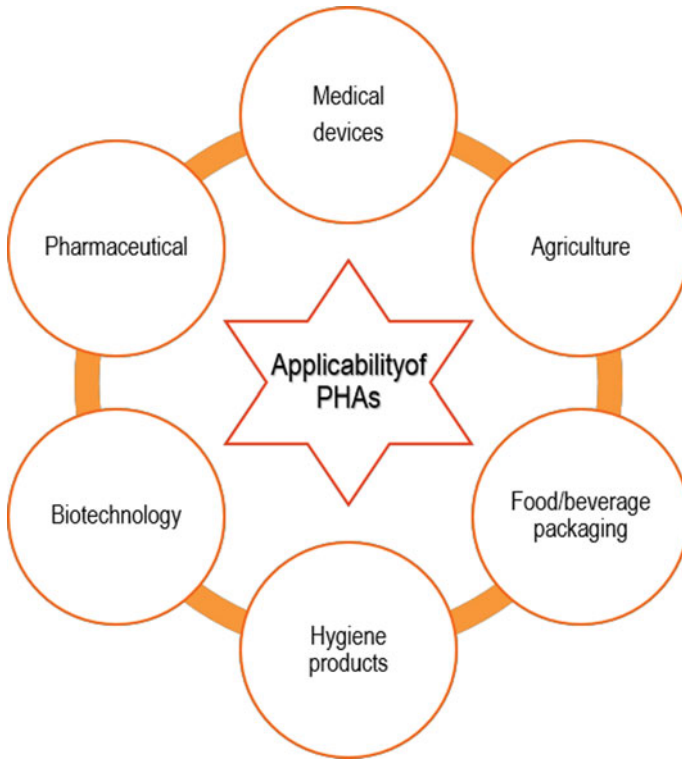


Fig. 2 Areas of PHAs applicability

137], and some illustrative examples of PHA-based reinforced nanomaterials for food/beverage packaging are being presented in Table 2.

3 Polyactic Acid (PLA)

PLA is a natural-sourced polymer conventionally (fermentation) or chemically indirectly synthesized from lactic acid, a bio-based monomer produced from agricultural wastes, like starch-rich products: corn, beet, rice, potato, sugar, sweet sorghum, tapioca, and wheat [1, 19, 45, 54, 72, 107, 137, 169]. PLA has attracted attentiveness in packaging for its special characteristics, such as chemical resistance; excellent transparency; flavor and odor barrier; relative moisture barrier; relatively high mechanical strength comparable to polyethylene, polyethylene terephthalate, and polyvinyl chloride; UV-light barrier properties, better than in low density polyethylene; flexibility, thermoplasticity, scalping resistance, and eco-friendly features (biodegradability, recyclability, monomer renewability, good processability, lower carbon footprint, and lower energy consumption) [50, 66, 76, 89, 110, 116, 139,

Table 2 Illustrative examples of food packaging bionanomaterials based on PHAs

Engineered BNC nanomaterials	Applications	References
[P(3HB-3HV)] /CNC/Silver	Food/beverage packaging	[167]
[P(3HB)] /PLA/CNC/Acetyl tributyl citrate	Food/beverage packaging (O ₂ barrier, UV-light blocking stretchability, thermal stability)	[12]
[P(3HB)] /CNC	Food/beverage packaging (Improved gas barrier)	[32]
[P(3HB-3HV)] /ZnO	Active food packaging (Optical and thermal enhanced features)	[25]
[P(3HB)] /Silver	Active food packaging (Significant antibacterial effect, without change in thermal stability or biodegradability)	[26]
PHAs/Nanoclay	Food/beverage packaging (Excellent mechanical improvements)	[42]

BNC—Bacterial nanocellulose

CNC—Nanocrystalline cellulose

PLA—Polylactic acid

PHAs—Polyhydroxyalkanoates

P(3HB)—Poly(3-hydroxybutyrate)

148, 166]. PLA, just like PHAs, is a contributor to the growth of natural-sourced biodegradable materials, but is biodegradable under industrial composting conditions, showing extremely little mineralization in most environments (landfills and ocean) [24, 27, 88, 89, 159]. In addition, PLA has the benefit of being compostable together with organic waste [23, 89]. PLA has potential for use in many areas, such as medical, pharmaceutical, foods and beverages packaging, agricultural and geotextiles sector, furnishings, apparel, and hygiene products [57, 64, 68, 71, 85, 86, 89], (Nurul et al. 2016) (Fig. 3).

3.1 Applicability of PLA in Food/Beverage Packaging

The great significance of PLA packaging is due to its special characteristics for sustainable packages (films, food service ware, containers, cold drink cups, trays, wrapping, bottles, foams, shopping bags) and coatings, being the cheapest bio-based material [17, 47, 63, 72, 74, 89, 137]. The PLA is GRAS (Generally Recognised as Safe) material and can be used in direct contact with drinks served under 90 °C [24, 89, 137]. PLA, as beverage packaging material, exhibits several limits because its brittleness, low gas/vapor barriers, low flexibility, thermal instability, and slow biodegradation rate, which can take up to 3–5 years [45, 66, 89, 124, 137, 138,

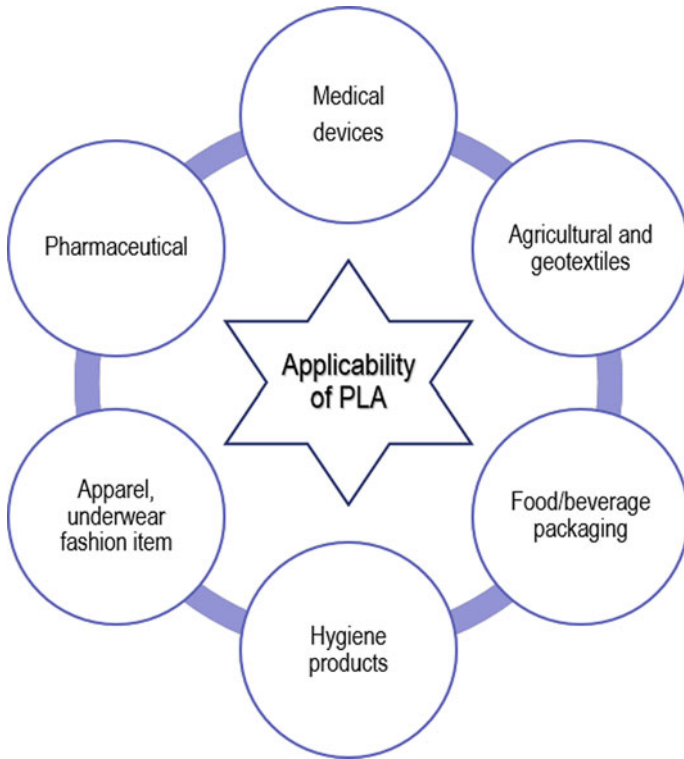


Fig. 3 Areas of PLA applicability

148]. Moreover, the use of bottles from PLA is restricted only to non-carbonated drinks because the PLA has low CO₂ barrier, which leads to beverages with an insufficiency of carbonation [24, 137, 148]. These PLA limitations can be overcome by using different ways, such as making composites/nanocomposites and coatings [31, 37, 56, 73, 77, 81, 89, 97, 103, 111, 115, 123, 146]. Some examples of PLA biopolymer composites for food/beverage packing are shown in Table 3.

Conclusions and Future Scope

Conventional petroleum-based packaging materials have preferential choice in food/beverage packing areas due to their relatively cheap, great transparency, flexible/rigid structures, and good mechanical properties. However, the most petroleum-based packaging materials are viewed as a source of pollution, having a negative influence on the environment, which needs to embrace more sustainable means of food/beverage packaging. From this perspective, the bacterial nanocellulose, polyhydroxyalcanoates, and polylactic acid seem to be excellent eco-friendly alternatives to solve the pollution environment problem. Bacterial nanocellulose possesses remarkable properties (biodegradability, renewability; green processing, and high mechanical properties thanks to the ultra-fine 3D nanofiber network structure),

Table 3 Examples of PLA composites for food/beverage packing

Engineered BNC nanomaterials	Applications	References
PLA/NC	Food/beverage packaging (Nanomaterial with improved oxygen barrier properties)	[39, 40]
PLA/Nanoclay	Active food/beverage packaging (Nanomaterial with improved water vapor barrier property and bacteriostatic function against <i>Listeria monocytogenes</i>)	[115]
PLA/Titanium dioxide	Active food/beverage packaging (Nanomaterial with enhanced thermal and mechanical characteristics, biodegradability, bacteriostatic activity, biocidal and antifungal)	[37, 73, 123, 170]
PLA/Cellulose/Nanosilver	Active food/beverage packaging (Nanomaterial good transparency, improved tensile strength, antimicrobial action for <i>Staphylococcus aureus</i> and <i>Escherichia coli</i> bacteria)	[38]
PLA/Silica	Food/beverage packaging (Nanomaterial with thermal stability, increased degree of crystallinity, enhanced mechanical and barrier features)	[15]
PLA/ [P(3HB)] /CNC/Acetyl tributyl citrate	Food/beverage packaging (Nanomaterial with improved crystallization, enhanced oxygen barrier characteristics)	[12]
PLA/CNC/Nanosilver	Active food/beverage packing	[44]

(continued)

Table 3 (continued)

Engineered BNC nanomaterials	Applications	References
PLA/Zinc oxide	Active food/beverage packing (Nanomaterial with good mechanical properties, gas decreased permeability, increased water vapor permeability, antimicrobial action for <i>Bacillus cereus</i> and <i>Escherichia coli</i> bacteria)	[77, 81]
PLA/Bleached bagasse carboxymethyl cellulose	Active food packaging (Packaging film for mango shelf life extended, good flexibility, improved moisture control)	[56]
PLA/Cocoa bean shells	Food packaging (Material with improved barrier properties, low levels of food migration)	[96]
PLA/Cellulose	Active food packaging (Compostable packages with high water vapor transmission rate)	[111]
PLA/Poly(butylene-succinate-co-adipate) /thimol	Active food packaging (Packaging film for bread fungal protection)	[146]

having various applications in different areas (medical/bioprocessing/pharmaceutical applications, additive in food, food/beverage packaging, cosmetics, environmental protection, textiles). In addition, the bacterial nanocellulose mixing with different compounds (nanofillers, bioactive substances) can enhance/share new functional characteristics (active, intelligent food packaging) to the bio-based matrix. These functional characteristics can open the market of bacterial nanocellulose packages as innovative nanomaterials in competition with fossil-based materials. Polyhydroxyalcanoates are long-term sustainable alternatives to conventional petroleum-based polymer materials thanks their eco-friendly characteristics, such as biodegradability, recyclability, renewability, lower energy consumption, and lower carbon footprint. Polyhydroxyalcanoates can be completely recycled into water, CO₂, methane, or biomass in various natural environments. However, they have some inherent limits (inferior mechanical/thermal stability, inferior moisture and gas barriers, and higher value for flavor barrier than petroleum-based materials). Shortcomings regarding these limits can be overcome by embedding several nanofillers into polyhydroxyalcanoates matrix, generating innovative functional nanomaterials for the food/beverage packaging sector. Polylactic acid is a safe and encouraging renewable biopolymer for

food/beverage packaging application, helping lowering carbon footprint and lower energy consumption during production. However, it exhibits several limits (brittleness, low gas/vapor barrier, poor mechanical properties, thermal instability, and slow degradation rate influenced by its crystallinity) and still needs to be enhanced. To counterbalance its limits, adding nanofillers produce functional eco-friendly composites, with enhanced biodegradability. The use of completely biodegradable biopolymers is expected to solve the solid waste and pollution problems caused by the fossil-based polymers, as well as provide a route to a circular economy.

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Sustainability Challenges and Future Perspectives of Biopolymer



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Abstract Biopolymer has become a significant alternative to conventional petroleum-based plastics. Over the years, ‘time and energies’ have been spent to sustain and modify these traditional biopolymers to make them more user-friendly and via designing novel polymer composites out of naturally occurring materials. These efforts have also been influenced by the idea that biodegradable polymer materials will reduce the production of synthetic polymer at very low cost, thereby producing a positive effect both environmentally and economically. This chapter discusses about the sustainability challenges of biopolymer production and future perspectives of biopolymer. The market growth and factors influence the demand of biopolymers that were introduced in several aspects: (i) cost and competition with existing synthetic polymers, (ii) facile production routes, (iii) availability of viable sources for biopolymers, and (iv) environmental aspect of biopolymer versus synthetic polymer and lastly the discussion of the future perspectives of biopolymer. Lastly, this chapter summarizes findings obtained in recent years, trying to identify open questions and future perspectives to overcome the present gaps and limitations.

Keywords Biopolymer · Sustainability · Challenges · Future perspectives · Polymer

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1 Introduction

As described in the previous chapters, biopolymers have been as the main interest among scientific community and industries [42]. As it is naturally produced by living organisms, hence it is said to replace petroleum-based products and can be applied in wide range of applications including material synthesis, biomedical applications [39], food industry [18], packaging application [2], water purification [7, 24], and enhanced oil recovery (EOR) [1, 3, 45]. As compared to plastic, which produces 300 million tons annually; the utilization of biopolymer up to this date is approximately less than 1% than the usage of petroleum-derived plastic. Nevertheless, its demand and production are steadily rising. In USA alone, the market of biopolymer increased from \$3.3 billion in 2012 to \$4.6 in 2016. In addition, it is forecasted that the global biopolymer market will grow from \$10.5 billion in 2020 to \$27.9 billion in 2025, with CAGR 21.7% within the 5 years period [9]. There are multiple factors that might contribute to the growing demand to utilize biopolymer. Some of these factors are as follows [22, 38]:

- (1) *Unpredictable oil prices.* Nowadays, synthetic polymers derived from petroleum such as polytetrafluoroethylene (PTFE) and epoxy have been widely used over the years. Synthetic polymers offer desirable properties such as chemical inertness, strength, flexibility, and resistivity. Yet, declining non-renewable oil and gas sources and unpredictable oil and gas prices had led to development of new alternative for these synthetic polymers.
- (2) *The global interest in using natural resources in various fields.* Compared to synthetic polymers, which are produced from non-renewable sources, biopolymers can be derived from wide range renewable and abundant sources, which attribute to their potential as replacement for synthetic polymers derived from petroleum. Packaging end use industry is the main key player that highly demands the use of bioplastic, which can replace conventional plastic for the making of bottles, cartons, plastic bags, films, food service ware etc.
- (3) *Concerns on greenhouse effect and carbon dioxide emission.* This concern arises because most of synthetic polymers release carbon into the atmosphere. Taking plastic for an example, the carbon food print may reach up to 6 kg CO₂/kg plastic [17]. This concern is also supported by government policies on green procurement and regulations which bans and implement additional charge per usage of conventional plastic.
- (4) *Current emphasis on waste management.* Nearly all conventional polymers are non-degradable. This can seriously affect ecosystem, wild and marine life, and human surrounding. On the other hand, most biopolymers and biodegradable; this will assist in preserving and conserving environments from pollution.

Following these factors, interests have sparked in producing and utilizing biopolymer as an alternative to synthetic polymers. However, there are some challenges that arise in the sustainable production of this type of material. Hence,

in this book chapter, focus is given to discuss about the sustainability challenges incurred in the production of biopolymers in various aspects and future perspective of biopolymers.

2 Sustainability Challenges of Biopolymers

In brief, production and market sustainability of biopolymers depend on few criteria. The utmost factors that need to be taken into consideration are (1) cost and competition with synthetic polymers; (2) large scale and facile production routes; (3) availability of viable quantities of renewable sources; and (4) end life treatment as compared to synthetic polymers. To be as a sustainable material, biopolymer should meet these four criteria.

2.1 Cost and Competition with Synthetic Polymers

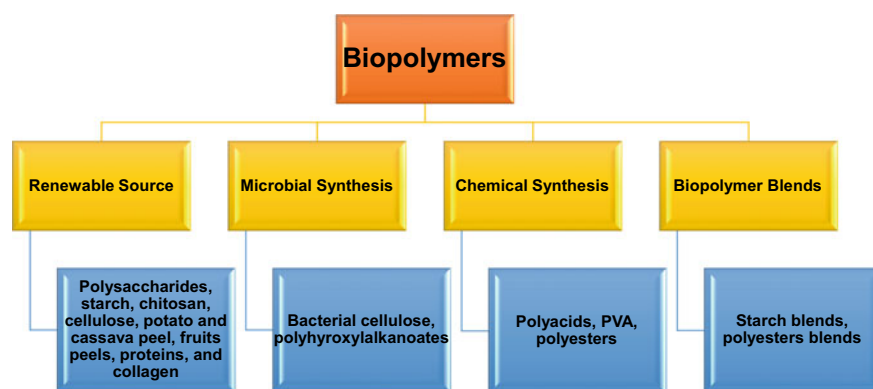
As compared to the conventional polymers, higher production cost of biopolymers stands as its utmost limitation. For example, while conventional polymers cost around USD 1000–1500/MT, even the production cost of commonly used biopolymer such as polylactic (PLA) cost at least USD 4000/MT and can reach as high as USD15000/MT for polyhydroxybutyrates (PHA) (biopolymer has good growth prospects in the world). Currently, it is reported that biopolymers are approximately up to 7.5 times more expensive than conventional petroleum-derived products. Hence, there many efforts have been carried on to develop such process that can reduce production cost of biopolymer. Taking PHA, PHB, and PLA as examples, the production of these biopolymers is commonly undertaken in batch fermentation process under the presence of bacteria that consumed large amount of organic carbon sources and salts; approximately attributed 50% of the production cost. Table 1 tabulates the challenges to produce cost competitive PHA as an example of emerging biopolymers and the upcoming solutions to resolve the limitations [12]. If these issues can be tackled, biopolymers can be as a versatile option to replace conventional polymers derived from fossil fuels.

2.2 Facile Production Routes

In general, there are various methods and techniques that can be used to produce biopolymers. Figure 1 shows the production process of biopolymers based on the desired end product and the available sources [33]. In brief, there are three main principle ways to produce biopolymer from renewable sources [8]:

Table 1 Issues and limitation of producing cost-effective PHA

Issue	Limitation	Solution
Process that requires high energy requirement	Caused by intensive aeration and sterilization procedures	Use less sterile and microaerobic process
Low conversion of PHA	Caused by unsuitable substrates and most substrates used for other purposes	Delete or weaken any unrelated PHA pathway
Structure of PHA is unstable	PHA is converted in multiple pathways within single process	Delete or weaken any unrelated PHA pathway
PHA production batch is unstable	Unstable activity of PHA synthase that convert PHA	Controls the activity of PHA synthase
Slow growth	Possible occurrence of binary fission	Use of multiple fission
PHA production process is not continuous	Possible occurrence of contamination during the process	Utilization of strains which resistant to contamination
Costly downstream process	Complex extraction and purification of biopolymer	Design of hybrid downstream strategy

**Fig. 1** Production sources of biopolymers

- (1) From readily available resources with partial modification (e.g., starch).
- (2) Production of biopolymer monomers by fermentation followed by polymerizations (polylactic acid, polybutylene succinate, polyethylene).
- (3) Microbial synthesis methods using various types of bacteria (polyhydroxyalkanoates).

Till today, various methods applied for the production of bio-based polymers are not sufficiently scalable to meet the market and the growing demand of biopolymers. Despite some biopolymers such as polylactic (acid) (PA) and cellulose have been produced at industrial scale, there are many other types of biopolymers that have not yet been commercialized. For an instance, PHAs have been reported to have great

potential as a replacement of petroleum-derived plastic; however, its commercialization is still hindered at research and development stage due to the high production cost of this biopolymer [35]. The high-cost production can be ascribed due to three main factors: (1) a very sterile condition is required to conduct batch/fed-batch microbial fermentation; (2) the use of costly carbon substrates that contributes to 40–50% of overall production cost; and (3) tedious and time-consuming downstream process for extracting and purifying PHAs. Changing the cultivation approach (as such using pure and genetically engineered culture and mixed microbial cultures), using cheaper carbon substrates and improving the downstream process of extraction and purification by implementing green and sustainable extraction process instead of using harmful and toxic solvents and additives may resolve these limitations [35].

As mentioned earlier, for the first factor, batch/fed-batch fermentation process is the current technique used to produce PHAs in which the cyanobacteria used in the process requires a very feasible and sterile mass cultivation system to prevent microbial contamination. For this concern, the growth of cyanobacterial should be properly carried out by controlling the abiotic factors such as temperature, concentration of nutrients, light, O₂, CO₂, pH, salinity, chemicals, and operational parameters such as shear stress, culture depth, rate of dilution, rate of harvest, and biotic factors such as presence of pathogens (viruses, bacteria, fungi) and competition with other non-related algae [43]. In contrast, continuous and open fermentation by using mixed microbial population (MMCs) can be one of the alternatives to synthesize biopolymer in much sustainable way. As compared to single pure strain such as *Cupriavidus necator*, MMCs do not require too sterile conditions. In addition, MMCs possess stronger metabolic potential and thus could reduce some cost at certain extent and permits many cheaper substrates. However, in certain cases, lower concentration of final product, much complicated downstream processes and difficult process designs. Yet, despite this, there are few studies reported such simultaneous and sequential production of biopolymers via this technique; however, these findings are only reported unplanned observation rather than any prior deliberate design. Prerequisite procedures that involve process parameters such as sufficient culture mixing, gas transfer, and optimal light condition shall be consistent during the production period.

Alternatively, genetic engineering and recombinant DNA technology may as well improve the production of high-quality biopolymer. Future industrial biotechnology shall focus on developing contamination-resistant strains such as from extremophiles family that is able to increase carbon substrates to be converted to biopolymers and possess ability to control the molecular weight of the biopolymers. Tripathi et al. [41] genetically modified *Pseudomonas putida* by weakening the β -oxidation pathway by deleting FadA and FadB to production of PHAs containing 3-hydroxyhexanoate (3HHx), 3-hydroxyoctanoate (3HO), 3-hydroxydecanoate (3HD), and 3-hydroxydodecanoate (3HDD) in the form of copolymer, blockpolymer, and homopolymer [11]. On the other hand, Kamravamanesh et al. [25] used UV light as mutagen to develop *Synechocystis sp. PC 6714* mutants for high production of PHBs. As compared to the control strain, the mutated species showed 2.5-fold higher PHB productivity.

In term of downstream process, the common procedures involve microbial biomass pre-treatment, polymer extraction, and post treatment, in which these processes consumed high production cost as high-energy demand and non-recyclable chemicals are used. In a reported procedure for an example, downstream steps of producing PHAs involve an optimal pre-treatment of MMCs under acidic condition followed by dissolve of polymers by using solvents such as acetone or chlorinated compounds to be fermented by MMCs and lastly treatment with additive to remove MMCs membrane and extraction of biopolymers within microbial cells. In general, the use of solvents assists in extracting high molecular biopolymers, but so far, a very low yield ranging from 18–30% was obtained. On the other hand, strong oxidants provide higher extraction yields (nearly 100%) but decrease the molecular weight of the biopolymers. Thus, if the downstream process can be optimized and sustainable process design is executed, this will optimally reduce the entire cost of biopolymer synthesis.

2.3 *Viable Renewable Sources*

Despite biopolymers are widely distributed in nature, very limited number of plants and animals are extensively being used in order to produce commercial biopolymers. In general, for the past years of research on biopolymer synthesis and production, the renewable carbon sources for biopolymers can be divided into three classes:

- (1) 1st generation: Trees and plants that contain high amount of carbohydrates and normally used as feed stock such as maize and sugar cane.
- (2) 2nd generation: Trees and plants which is not being used as feed stock but rich in carbohydrates which commonly waste materials from the 1st generation feed stock such as bagasse, husks, sawdust, and bone waste.
- (3) 3rd generation: Carbon sources derived from algae that has higher yield than the 1st and 2nd generations.

For the first-generation, starch obtained from feed stock plants are often extracted to produce commercial polymers where these sources and species are usually genetically modified in order to obtain higher yield [8]. Thus, because of growing demand of biopolymer, the expansion of cultivable land area increases. Due to the concern of the first-generation sources that affect human feedstock, the future prospect is now focusing on the use of agricultural wastes, food wastes, or waste from wastewater as second-generation biopolymer sources.

Due to the concern of the first-generation sources, the future prospect is now focusing on the use of agricultural wastes or waste from wastewater as second-generation biopolymer sources. In addition, Food and Agriculture Organization of United States reported that almost one over third of about 1300 million tons of food is wasted yearly [5]. This being as the main factor to utilize these agricultural and food wastes to turn into valuable biopolymers. Figure 2 shows wide range of agricultural and food waste that can be used as renewable sources to produce biopolymers with

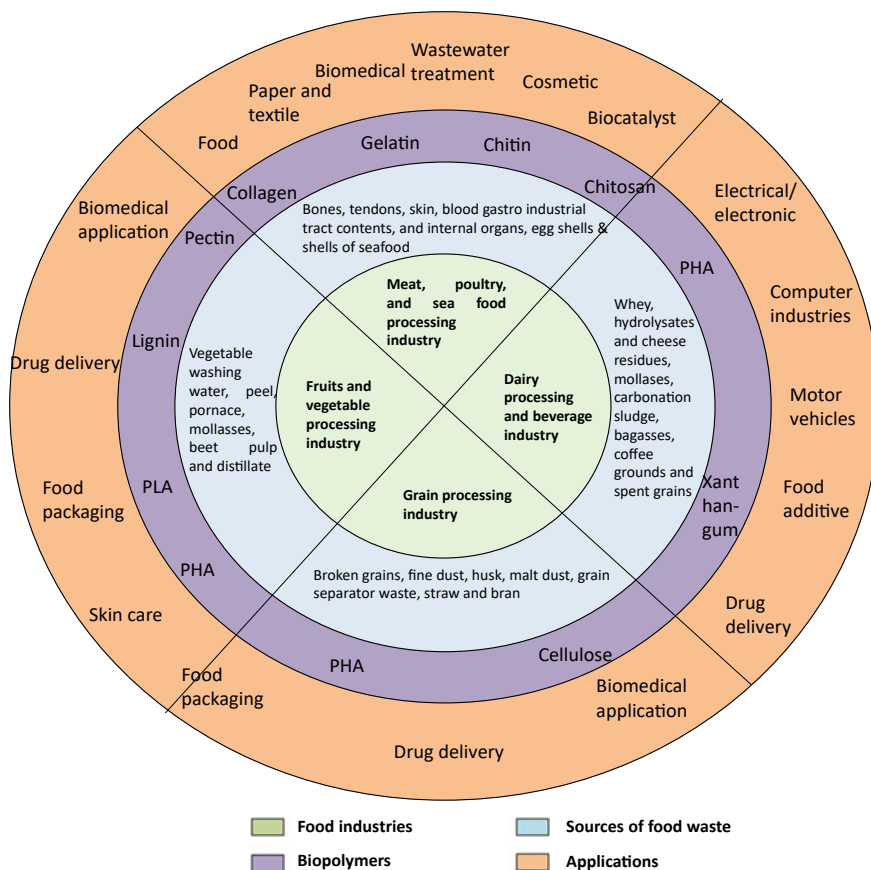


Fig. 2 Different second-generation sources of biopolymers and their applications [37]

a wide spectrum of chemical and mechanical properties. In general, few of them have been studied, meanwhile many more of them still require further exploration for suitable extraction technique and applications.

Different production of biopolymers produced by different types of agricultural and food wastes is tabulated in Table 2. Based on the table, abattoir waste especially cattle and pig skins, bones, fish scale, etc. becomes the main source to produce collagen, chitin, and chitosan for food, biomedical, pharmaceuticals, cosmetics, and leather industries [28]. On the other hand, cellulose, pectin, PHA, and hemicellulose are produced from various lignocellulosic biomass, fruit peels, rice husk, protein whey, and many more. Their production is mainly generated by enzyme-catalyze polymerase reaction, during complex metabolic processes under natural conditions or via microbial fermentation synthesis [37] (Table 3).

Table 2 Production of different biopolymers by using agricultural/food wastes

Types of waste	Waste products	Food industries	Type of produced biopolymers	References
Abattoir waste	Bones, tendons, skins, contents of gastro industrial tract, blood and internal organs, eggshells, shells from seafoods	Meat, poultry and seafood processing industries	Collagen, gelatin, PHA, chitin/chitosan	[30, 36]
Waste from rice mills, grist mills, malt house	Broken grains, fine dust, husk, malt dust, grain separator, waste, straw, bran	Grain processing industry	PHA	[6, 21]
Waste from milk and cheese production	Whey, hydrolysate and cheese residue	Dairy processing industry	PHA	[14]
Waste from preparation and processing of fruits, juice, industries oil mills	Vegetable washing water, peel, pomace, molasses, beet pulp, distillate	Fruits and vegetables processing industries	PHA, pectin, lignin, cellulose, PLA	[31, 40]
Waste from production of alcoholic and non-alcoholic beverages	Molasses, carbonation sludge, bagasse, spent grains, tea and coffee grounds	Brewery and beverages industries	PHA	[16, 26]

2.3.1 Algae as the Latest Promising Biomass Source to Produce Biopolymer

Apart of agricultural and food wastes, nowadays, much attention has been given to algae as carbon source to produce biopolymer. There are many studies and reviews that have reported the advantages of using algae as the biomass source for biopolymer production. In general, algae retain very high biomass productivity ascribed by its superior CO₂ uptake (approximately 1.8 lb) and able to release 75% O₂ to the surrounding environment [27]. As compared to the first-generation that require large cultivation land and second-generation that highly depended to the mass production from the first-generation source, the cultivation of algae is much convenient and does not require any cultivation land that might interrupt the production of human feed stock. Algae can be conveniently cultivated in such harsh environment, which use wastewater as the source.

For the case of biopolymer production from algae, it contains high amount of starch and cellulose, which can undergo fermentation to produce different classes of biopolymers such as polyolefins, polyamide, and polyesters. In addition, natural

Table 3 Properties of some common algal biomass

Algae	Class	Protein content (wt%)	Carbohydrate content (wt%)	Lipid content (wt%)	Carbon	Hydrogen	Oxygen	HHV	Features	References
<i>Ulva prolifera</i>	Macroalgae	–	–	–	35.2	5.6	51.6	11.1	Good source of energy, high content of alkaline and earth metals	[23]
<i>Ulva prolifera</i>	Seaweed	–	–	–	37.44	7.01	50.8	16.54	High HHV, resistant to different environmental conditions, low maintenance requirements	[10]
<i>Eklonia radiata</i>	Seaweed	7.6	65.4	3.6	32.6	5.1	50.8	16	Low carbon content, low phlorotannin content, high glucose and fucoidan contents	[46]
<i>Undaria pinnatifida</i>	Seaweed	12.5	55.9	2.2	34	4.6	46.5	17	High protein content, high monosaccharide yield, rapid growth rate, high productivity	[46]

(continued)

Table 3 (continued)

Algae	Class	Protein content (wt%)	Carbohydrate content (wt%)	Lipid content (wt%)	Carbon	Hydrogen	Oxygen	HHV	Features	References
<i>Nannochloropsis sp.</i>	Microalgae	31.68	8.99	15.035	–	–	–	–	Excellent source of protein, good nutrient content, good productivity, high hydrocarbon content	[20]
<i>Botryococcus braunii</i>	Microalgae	70	–	–	77.04	12.4	9.86	35.6	High hydrocarbon content	[44]
<i>Spirulina</i>	Microalgae	70.3	23.9	5.8	46.9	6.9	35.5	18.5	High energy recovery rate	[19]
<i>Chlorella</i>	Microalgae	50.2	41.92	3.22	49.27	7.01	35.59	24.6	High HHV and high protein content	[4]

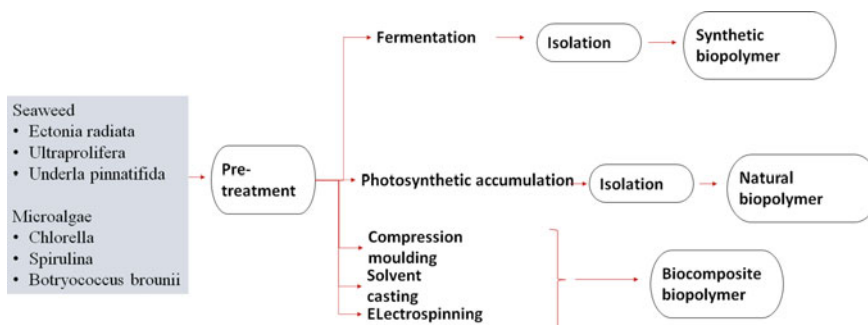


Fig. 3 Production of biopolymer from different type of algae

polymers from algae biomass are proved to be less toxic, biodegradable, higher strong, and tensile property as well as possesses anti-microbial, anti-tumor, anti-oxidant, and immunomodulatory features. So far, among 72,500 algae strains, 36,250 strains have been studied for various applications, and Table 2 shows some of reported strains of algae which can be potentially used for production of biopolymer [32].

From Fig. 3, it can be seen that the production of biopolymers from algae is usually conducted by fermentation process by using microorganism, naturally produced inside algae cell factories by photosynthesis process and through combination with additives to produce composite biopolymer. For the first route, the fermentation is carried out by using algae producing enzyme that can convert algal biomass to potential biopolymer [29]. For second route, modified light source such as adjusted UV irradiation is required so that photosynthesis process can occur [15]. Any modification of the light intensity results to specific extraction of polysaccharides, lipid, and lignin, which act as precursor of biopolymer. Meanwhile, the third route is usually to produce algae-polymer blends by compression methods in which algae and additives are compressed in a mould [13]. Solvent extraction, microwave assisted extraction, and subcritical water extraction are three common methods to isolate biopolymer from algae [27].

So far, these highly potential algal species can be effectively grown in closed photobioreactors. The most suitable photobioreactors such as tubular photobioreactors, plate reactors, and bubble column reactors can be used for mass cultivation of algal. One of good example of photobioreactors is The Photon System Instrument, which is developed in 2015. This photobioreactor is equipped with flat panel system and can be adapted according to the required cultivation process (end product, strains, and species). Apart from this, an ideal photobioreactor shall provide the best solution to allow viable phototrophic cultivation for various cyanobacterial and algal strains. Nevertheless, so far, the development of ideal photobioreactor is still on going.

2.4 Environmental Aspect of Biopolymer Versus Synthetic Polymers

Based on Life Cycle perspective, biopolymers enable the diversion of water from landfills where 80% of petroleum-derived polymers are unable to do so. In this perspective, carbon cycle can be reduced as the sources of biopolymer are renewable and any disposal of biopolymer will not cause any harm to the environment as it can be degraded in the form of energy or compost product which can be recycled by soil and plants. According to European Research, starch-derived polymers offer better CO₂ emission of 0.8–3.2 tons CO₂/biopolymer plastic and energy saving of 12–40 GJ/ton bioplastic as compared to a ton of petroleum-derived polyethylene-based plastic. Recently, The National Institute of Standard (NIST) suggested that in comparison to petroleum-based polyol (components of polyurethane), polyols derived from soy plants only attribute to one over four environmental impacts. Through the utilization of biopolymers, smog formation, global warming, ecological toxicity, and consumption of fossil fuel can be reduced.

Despite most biopolymers are biodegradable and environmentally friendly, some of them in fact require a very long duration to decompose in the natural environment. For example, in a controlled composting environment, it may take about three months for PLA to break down into its constituent parts. However, if the environment is not controlled, and there is no presence of light and oxygen, as long as 100–1000 years is required to decompose a PLA bottle. If the product is composed in between biopolymer and synthetic polymer (e.g., PLA and PET), there is no optimized method of separating PLA from PET that has been reported yet. In addition, the non-common separation technology will incur high cost and reduce the recycling value of PET [33]. So far, the use of PLA has been against by many environmentalist and recycler, unless if proper technology to completely remove PLA can be introduced.

In addition, for bioplastic-derived biopolymer, The European Plastic Recyclers Associations has raised concern about the potential of bioplastic to do more that to the environment than the current used plastic. Besides that, for real application, there are reports of the quality issues of biopolymers. In comparison to petroleum-derived plastic, biopolymer possess lower physical, mechanical, and chemical resistance [34]. In addition, some biopolymer-based plastic is highly brittle when exposed to water vapor and oxygen, making them unsuitable consumer applications.

3 Current Status

Previously, petroleum-derived polymers have been widely used in various applications. However, several factors such as uncertainty of oil prices, environmental considerations of using petroleum-derived biopolymers, technological advancement

of biopolymer production, and accelerated innovations of biopolymer-based products lead to growing demand of biopolymer. To be at par with petroleum-derived biopolymers, some challenges such as sustainable production of biopolymers, in particularly in term of production cost, economic large scale production process, and management of raw biopolymer sources should be addressed.

In order to make biopolymer to be economically viable, it is very crucial to develop: (1) logistic biomass feedstock, (2) alternative for sustainable food or agricultural waste for biopolymer feed stock, (3) new manufacturing routes or improvement of techniques for higher yield of biopolymer production, (4) alternative of new strains/algae/mixed strains that can effectively synthesize biopolymer and at the same time can be easily cultured and grown, and (5) efficient downstream process method to reduce the entire production cost involved.

Despite some biopolymers are produced in industrial scale, several factors still need to be considered for the long-term viability of the bio-based polymers. It shall be noted that the renewable feedstock used for production of biopolymers is often competing with the requirement for food-based products for human consumption. In general, the expansion of first-generation feed stock crops is the threat of sustainability of biopolymer. Hence, focus should be given to second-generation and third-generation biomass. Considering that there are many types of different food wastes and agricultural wastes, focus should be given to the exploration of each of these wastes and the design of suitable approach for the production of desirable biopolymers. Considering the global variability in the availability of agricultural waste, the development of the materials would be concentrated in specific geographical areas.

Major limitation of some new biopolymers is that they are unable to be processed in a standard process. Previously, there is vast knowledge that has been implemented on addition of additive and modification of routes to improve the performance and processing of fossil fuel biopolymers; this knowledge can be implemented to the synthesis of biopolymers to meet similar properties to the established petroleum-derived polymers. For an example, new grades of PLA with higher thermal and mechanical properties have been introduced by Nature Work LLC, which this PLA-tri block copolymer behaves like thermoplastic elastomer. Apart of that, many other developments have been currently on going for other types of biopolymer such as polyamides, polyesters, and PHAs with tailored properties to be used in specific automotive, electronic, water/wastewater, biomedical, and food packaging applications. One of the innovative approaches is by blending the biopolymer or using nanoparticles as additive to improve the performance of new functional biopolymer. Incorporation of various nano-reinforcement fillers such as carbon nanotubes, graphene, nanoclays, inorganic nanofillers, 2D and 3D nanofillers, and other strong biopolymers could enhance the physicochemical properties including thermal stability, rate of biodegradability, mechanical and chemical stability, solvent uptake, flame resistance, etc. Nevertheless, the market of biopolymer as additives is still new and small, thus major research and developments need to be justified and taken into consideration by the manufacturing companies.

Much advanced methods involving genome sequencing should be further explored to generate customized bacterial biopolymers such as PHB and PHA from recombination of *E. coli* or other microbes as unadulterated cultures were associated with higher volumetric productivity and high costs. In contrast, poor yield is often reported despite this technique is affordable. Hence, another technique such as genetic engineering can lead to the design of suitable microbes for higher yield of biopolymer production. Advanced genetic methods can also be utilized to customize different strain of algae or raw materials sources of biopolymers. Apart from that, standard organizations such as ISO have published methods for material testing on biopolymer materials for sustainable development. As based to the nature and features of natural materials, more consideration and observation should be given to biopolymers rather than to fossil-derived polymers. Driven by these factors, biopolymer industry is expected to bloom. Thus, biopolymer industry has a great positive future, which is driven mainly by the environmental and economic benefits of using natural resources for production of biomaterials.

3.1 Conclusion and Future Scope

This chapter discusses on the sustainability challenges involved during the production of biopolymer in various aspects; cost and competition with synthetic polymers, production routes, viable renewable sources, environmental aspect of biopolymer vs synthetic polymers followed by future perspectives of biopolymers. There are several factors that accelerates toward the advancement of using biopolymer in various industries such as uncertainty of fossil fuel prices, alternative replace petroleum-based products into greener and natural resources, and environmental impacts of petroleum-derived polymers. Despite there are biopolymers that are commercially available, the production of potential biopolymers is hampered due to high production cost, non-scalable and economical production technique, and insufficient viable renewable sources. In the future, some alternatives can be conducted in order to maximize the sustainable production of biopolymer to meet with the growing market demand. This might include the development of biopolymer composite materials by incorporation of alternative materials that has main feature of biodegradability and offering competitive to current material costs. Subsequently this will not only solve the issue on sustainability of biopolymer, but it will also result at decreasing the amounts of plastic waste, less aggressive environment for product manufacturing as synthetic plastics are difficult to recycle and most importantly this protect nature for over a century.

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Biomaterials in Coating Industries



Zahra Ranjbar and Behnaz Ranjbar

Abstract Bio-based coatings are an emerging market with rising ecological concerns and increasing awareness for eco-friendly products. Compared to their petroleum-based counterparts, the bio-based material as formulation ingredients may reduce greenhouse emission and VOC content, decreased human or environmental toxicity, improved functions, and an appropriate cost-performance ratio. Bio-based ingredients for paints and coatings formulations, i.e., sustainable film formers/resins, additives, pigments, and solvents, are introduced during this chapter. In most cases, using bio-based raw materials leads to a successful formulation besides biodegradability, biocompatibility, lower disposal, and special purposes properties, i.e., antibacterial, thermal resistant, etc., compared to conventional materials.

Keywords Bio-based coatings · Bio-based resins · Bio-based pigments · Bio-based additives · Bio-based solvents

1 Introduction

The coating industry is under increasing pressure to moderate the environmental issue. Drivers are specifically the growing request for organic and ecologically harmless products and ecological and resource-saving manufacture approaches. The usage of bio coatings contains metal, cork, stone, and mainly wood surfaces. Bio-based coating products introduce a brand new fortuitous for the industry. Bio-based coatings have a major role within the coatings industry, although the prevailing market portion is estimated at about 5% of sales. Mostly these materials are additionally

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likely to achieve from long-established usual raw supplies [1]. The emerging bio-based raw materials have led manufacturers to look at their formulations closely so as to use more bio based materials. A typical coating formulation commonly consists of four major ingredients (Fig. 1).

Researchers have generally identified resins as a main part of coatings with a good potential for replacing petrochemical solutions with bio origins. These types of resins are partially or entirely supported raw materials that are made of biological resources [2]. These resins have a chance for replacement of traditional ingredients with the plant and natural-based alternatives. The foremost common plant and natural sources for bio-resins preparation are vegetable based materials like soybean and corn derivatives. Other plant based candidates include sugarcane, potatoes, sugar beets, cellulose, castor beans edible nut shells, derivatives. The plant-based materials in coatings are not a recent progress although the bulk of produced varnishes and paints are based on petroleum based raw materials (Fig. 2).

True is time to start changing. During recent years' novel bio-based resins are moving fast into the main path. Bio-compatibility and applicability of current uses of biomaterials permit revision of characteristics to boost efficiency during a biological resource whereas holding general characteristics of the popular coatings. Resins and binders are the foremost important part of a coating because they make the final film. Moreover, they will fix other component like pigments and additives within the vehicle by cohesive and adhesive forces. Commonly organic materials like polymers and resinous and barely inorganic or hybrid materials are used as binders in coating formulations whereas polymeric materials are preferred.

2 Film Formers/Resins (Binders)

All synthetic petroleum-based film formers/ resins are non-biodegradable and persist as there, even after their supportive deal, for an extended time. These non-biodegradable resins origin difficulties like waste removal and danger for eco-system, thus producing overall opposing ecological effects. Additionally, all of those polymers are commonly gained from natural resources like petroleum and have the chance of the reduction of investments. Accordingly, researchers and businessmen are yearning for another renewable, environmental, and economical asset to moderate need on natural sources, permitting non-renewable resources preserve to be deposited for the next generations. Naturally based raw materials like cellulose, lignin, and oil are utilized for several applications. These kinds of natural resources are recyclable and ecologic, accordingly, they are utilized in a wide variety of areas, particularly in coatings and packaging [3]. Bio-based resins are high molecular weights macromolecules. They carry covalent bonds of the many small repeating units. As this repeating units are numerous, adding or eliminating of some units does not have significant effect on final properties. These resins are categorized consistent with primary groups, techniques of preparing, etc. Biochemical procedures make these resins with or without unique enzymes or catalysts. Bio-based resins are largely

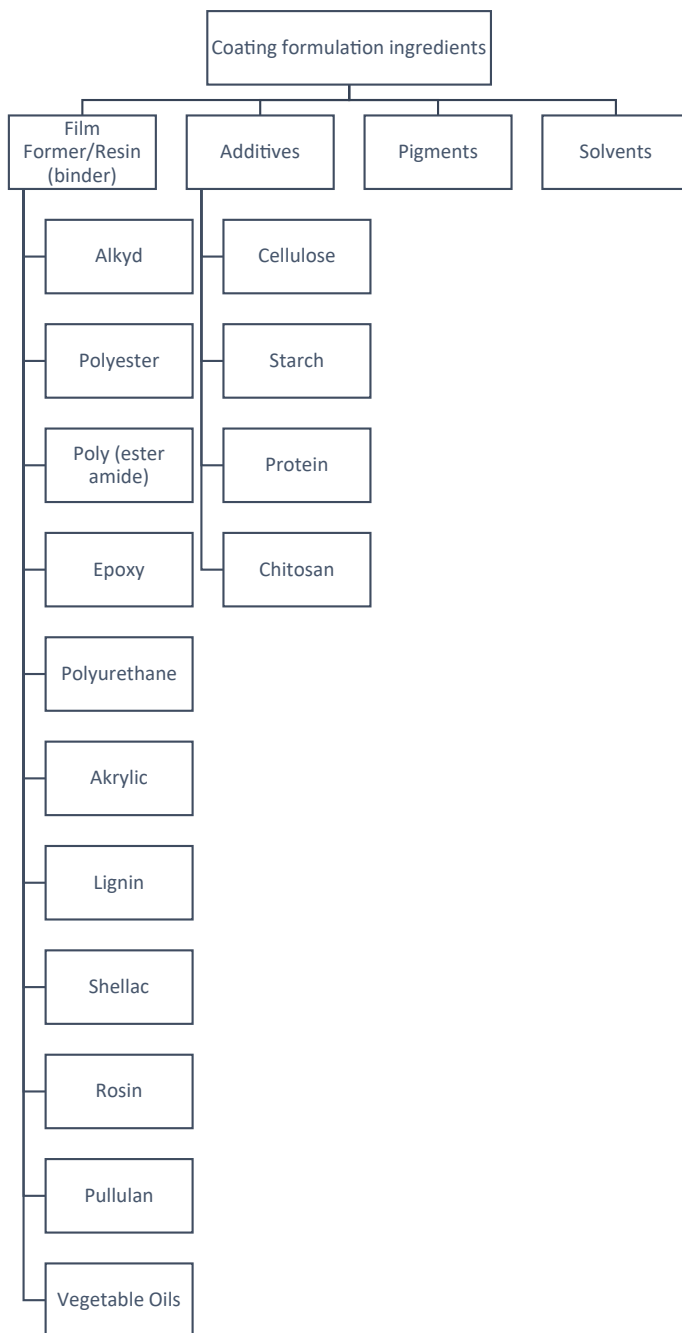


Fig. 1 Major ingredients in a typical formulation

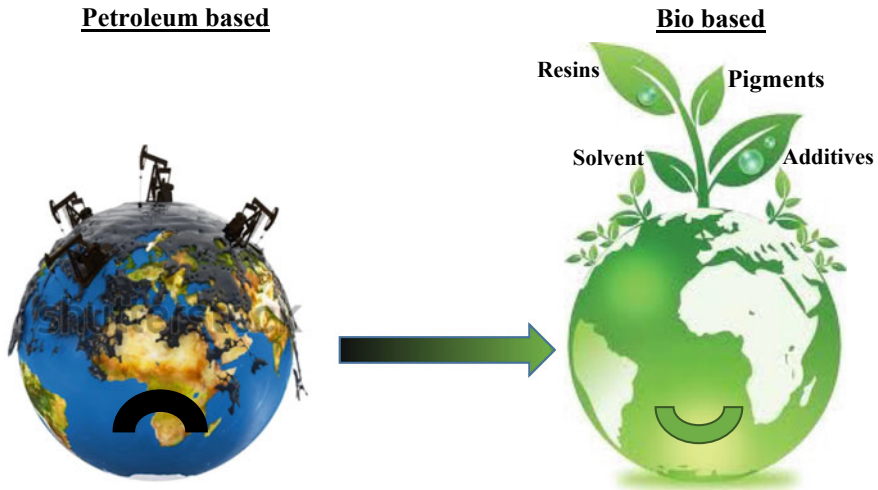


Fig. 2 Petroleum based versus bio-based paints and coatings

extracted from the resins gained from natural resources like agriculture's product or forestry. They will play like usual synthetic resins with biodegradability individualities upon removal. These resins are the so-called bio-derived or bio-based resins. Bio-based resins employed in coatings are certainly derived biodegradable resources [4]. These bio-based resins commonly undergo substandard mechanical properties, containing dimension constancy. "Bio-derived resins," like resins made from oil, edible nut shell liquid, and tannin, are flexible, and moreover, their functionality is treated providing that the desired properties are achieved.

There has been a rising attention in consuming bio-based film former building blocks to manufacture resins to be used in coatings in latest years. Bio-based produces are resulted from plants and other renewable agricultural, marine, and forestry supplies and substitutes to usual petroleum-derived products. The varied categories of bio-based film formers and resins for coatings are discussed within the following parts.

Superior consideration is given to broadening the spectrum of bio-based film formers and faster admission to raw materials, and observing for easier transport methods. The plant oils demonstrate exceptional properties regarding their fatty acid structures. The high amount of unsaturated fatty acids guarantees quick-drying, new performance, and a stimulating thanks to progress coating functionality.

The conventional and bio-based alkyds, epoxies, poly (ester amide) s, polyurethanes, polyesters, and acrylics utilized for preparation of coating materials are bio-derived materials.

2.1 Alkyd

Having over 50% of natural oils and carboxylic acids from renewable plant bases, alkyd resins are a rational option for supportable coatings compared to other petrochemical-based resin classifications. Resulting a failure period, the alkyd coating market has become stable in recent years and is presently delighted in a very period of modest development. As a carefully confirmed technology, alkyds proposal several performance profits that make them a nice-looking option for coating formulators, mainly wood applications. This is often because the drying time is long enough to let the diffusion into the wood substrate occur. Low VOC, solvent-borne resins are extensively accessible, as are water-based systems whose act is continually enlightening, with the additional benefit of greater ecological authorizations.

Alkyd resins have extensively been documented for green identifications which supported the natural fatty acids and polyol content that substituted most resin. In years of 1930s, alkyds had expanded a standing for prime quality, shiny appearance because of their low relative molecular weights. The oxidative drying also delivered good hardness growth and corrosion resistance properties. Within the 1950s, vinyl and acrylic resins were prepared via emulsion polymerization technology. This kind of polymerization technology made it probable to create water-borne products with better clean ability and less expensive to supply because of lower basic oil fees. These new water-borne coatings took the bulk of the architectural paints market.

An alkyd can be up to 100% bio-based and accomplishment. The critical components that frame an alkyd are fatty acids, di-acids, and polyol. All three can possibly become from natural non-fossil resources [5]. Resin manufacturers provide this molecule and, along with any agreed di-acid or fatty acid, combine an alkyd with specifically provided properties. The choice of the stuff is critical because it controls the drying and final properties. As an example, the fatty acid used defines the extent of yellowing and hardness improvement. Initial hardness is related to the resin's relative molecular weight and, consequently, to the di-acid and/or polyol. Thus, bio-based pentaerythritol is an excellent structure block because it facilitates to urge 4 primary hydroxyl groups with a 3D arrangement.

2.2 Polyester

Unsaturated polyesters are co-polyesters synthesized by condensation polymerization of a saturated/unsaturated dicarboxylic acidanhydride with di-alcohols. Afterward, the residual c–c double bonds of the ester condensation reaction can perform polymerization to provide a greatly cross-linked network. Unsaturated polyesters are generally formulated in sheet molding compounds, fiber-glass composites, and bulk molding compounds. They enjoyed long-term headship in traditional petroleum-based composites since 1941 thanks to their good cost to property ratio, comfort of transferring, and sufficient mechanical, heat-resistance, chemical and electrical properties [6, 7].

Recently, bio-based di-ols and di-acids having unsaturated functional groups have typically been accustomed make biodegradable-based unsaturated polyesters. Itaconic acids are a probable substitute to maleic anhydride and maleic acid. Reactive $C=C$ double bonds were placed within the backbone of polyester via the condensation reaction between 1,4-butanediol, itaconic acid/maleic acid, and succinic acid.

Bio-based polyesters are attractive in paint industry due to reactants availability, dispersability, straight forward preparation methods, proper adhesion, good gloss, and weathering resistance of the products. Many kinds of vegetable oils may employ in preparation of different kinds of polyesters. There are three types of polyester or alkyd resin: short oil, medium oil, and long oil. Different types of fatty acids, vegetable oils, and their derivatives are used for synthesise of polyesters, like polyhydric alcohols, diacid, and monoglyceride. However, mono-basic acid is optional and is merely accustomed control molecular weight/ viscosity or improve the structure of prepared polyester. Several catalysts like base, acid, or enzyme accelerate the polyester reactions. These include sodium methoxide, lithium hydroxide, dibutyltin, calcium octoate, and lipozyme. An outsized type of vegetable oil-based polyesters is reported within the literature using different vegetable, with sort of structures and compositions together with different di-polyols and di-polybasic acids [8]. A great range of polyesters prepared by bio-based fatty acids is presented in researches utilizing different vegetable oils with kind of configurations alongside with different dipolybasic acids and dipolyols [8].

Different types of bio-based unsaturated polyester resins were manufactured from itaconic acid and some different diols from renewable materials. UV curable water base networks of polyesters were synthesized. Their general and mechanical properties, heat stability, hardness, water and solvent resistance, flexibility, and adhesion of the prepared coatings were studied. Results revealed that the coatings based on UV-cured polyester showed high hardness and reliable water and solvent resistance [9].

2.3 *Poly (Ester Amide)*

To preserve a versatile coating with sufficient alkali resistance of bio-based polyester, amide links should substitute rather than some ester bonds in polyester. Therefore, these kinds of bio-based resins are gained from different vegetable oils and enjoy both amide and ester bonds in their structure. The amide bonds deliver stiffness as polyamide and versatile like polyester. Hence, poly (ester amide)s bring both inside one polymer. Therefore, bio-based poly (ester amide)s demonstrate superior function regarding weathering and heat resistance, hardness, physico-chemical and mechanical properties, over the polyesters which are bio-based [10].

A lot of vegetable oils and unsaturated fatty acids like linseed, castor, sun flower, Karanja, safflower, coconut oils, and their fatty acids, like linoleic, linolenic, oleic, palmitic, stearic, are wont to prepare the bio-based composite, di-hydroxy fatty amide for poly(ester amide)s. the opposite constituents of poly(ester amide)s are dibasic

acids or anhydrides near polyesters, di/polyhydroxy amines also as di-ethanol amine, hydroxymethyl amino propanol, and di-isopropanol amine. The catalysts which are used in this production are the same as polyester production.

2.4 Epoxy

Epoxy resins market cover approximately 70% of the thermoset resins. Diglycidyl ether of bisphenol A (DGEBA), which embodies quite 90% of the epoxy originators in the world, is out and away the foremost broadly monomer to organize epoxy networks. DGEBA is formulated from bisphenol A and epichlorohydrin with company of sodium hydroxide. Though epichlorohydrin will be prepared from bio-based glycerol, bisphenol A, consisting of over 67% of the DGEBA molar mass, is resulted from un-renewable resources. Moreover, bisphenol A has health problem for infants and children at low ages. Some of the developed countries have newly proscribed its applications in packaging for foods, particularly bottles for babies. Nowadays there has been growing attention in in evolving plant-based epoxy resins as substitutions to DGEBA. Plant oils are commonly utilized because the initial materials for lubricants, surfactants, resins, cosmetic products, and coatings because of their triglycerides that have the C link. C = C double bonds, plant oil, is transformed to epoxy resin by the epoxidation reaction with peroxide by chemo-enzymatic reactions and molecular oxygen [11, 12].

Epoxy resin is considered as an engineering material thanks to its sufficient properties like high dimensional stability, high mechanical and adhesive strength, low or zero shrinkage during curing, high chemical resistance, and high thermal stability. Epoxy resins are the organic low or relatively high molecular weight compounds with a minimum two epoxy groups in each molecule. Because of the highly strained three-member oxirane ring of epoxy binder, it is shown to be very reactive; therefore, a range of curing systems are used to get the required thermosets. Then, there is significant interest in epoxy thermosets due to their being cost effective, remarkable characteristics, and considerable reactivity toward different chemicals and also notable formulation variety to provide many significant properties. However, high flammability, inherent brittleness, and low toughness restrict the thermoset to utilize as a sole component in surface coatings and paints. Hence, some flexible polymeric binders such as poly(ester amide), polyester, and polyurethane are employed in combination with them. During this respect, vegetable oil-based epoxy has excellent adaptability with the polymers mentioned above and leads to better surface wetting of other components which exist in the coating systems.

Bio-based epoxy resins are prepared by direct epoxidation of unsaturated fatty acids or unsaturated vegetable oils by in place produced peracids like peracetic acid, performic acid, and perbenzoic acid. With or without of common aromatic diol, like bisphenol-F, bisphenol-A, tetra bromo bisphenol-A, bisphenol-H, bisphenol-S, and bis(hydroxyl phenyl) methane, in alkaline solution, monoglyceride polycondensation of the edible fatty amide diol or fat with epi-chlorohydrin caused the second

epoxy style. Sodium/ potassium hydroxide, sodium/potassium/ calcium carbonate, and potassium bicarbonate are used as catalysts. Many vegetable oils as sun flower, Karanja, castor, cotton-seed, soybean, Ferrera, and linseed oils are utilized for manufacturing of these kind of bio-based epoxies. Moreover, Vernonia oil formed by Vernonia galamensis and so is feasible to be employed in industry. Though, epoxidized vegetable oils cannot be made thermoset with preferred properties due to their low epoxy content. Besides that they need low viscosity and pretty high reactivity thanks to an epoxy group; thus, they are mostly utilized as a plasticizer and reactive diluent s for low-VOC and high-solid epoxy based coatings.

In literature, acrylated soya oil was utilized as a modifier for DGEBA-type synthetic resin [11]. The epoxy resins cured with different hardeners (MNA-methyl nadic anhydride, SAc-sebacic acid, PhA-phthalic anhydride, SA-succinic anhydride, MA-maleic anhydride, MXDA-m-xylene diamine, cycloaliphatic polyamine Epamine PC 17, MI-2-methylimidazole, and polyamide type Crayamid) were analyzed by Fourier transform infrared spectroscopy). To study the curing agents' effects, a subtle investigation was also done on the mechanical characteristics and hardness of neat epoxy resin. Comparison between the mechanical characteristics of the epoxy systems confirmed that the neat epoxy resin system had higher elongation modulus and tensile strength than that of M-ERs, which divers with the elongation at break. Higher tensile of 53 MPa and 58 MPa was detected for M-ERs cured with MXDA and MNA curing agents, correspondingly. A broad study of the mechanical and water sorption properties of M-ERs showed that for an epoxy system improved with AESO in 50 weight percent, MXDA and MNA were more operative hardeners. Coatings gained from M-ERs cured with anhydride-type hardeners were firmed to be considerably proof against corrosive acidic media.

2.5 Polyurethane

In organic coatings, polyurethane (PU) coatings have brilliant toughness, low-temperature flexibility, abrasion, corrosion, and chemical resistance, therefore getting utilized in numerous automobile finishing usages, industrial maintenance, and chemical resistance. There is a substantial attention in formulating polymers from renewable resources, for example, plant-based polymers derived from living organisms like trees, plants, and algae, since as decreasing non-renewable feedstock. Furthermore, plant-based polymers are shown to have plentiful profits, like their plentiful obtainability, cost effectiveness, and environmentally gentle. Two main bio-based resources exist in large quantities on the world are vegetable oils and cellulose. Vegetable oils are mostly wont to formulate polymeric binders for resins, coatings, and flooring materials while the usage of cellulose in polymeric coatings is proscribed. Within the recent years, oils and fats of vegetable and animal resources have also been utilized because the ascending requirements of renewable raw materials for producing fine chemicals within the industry. Generally, vegetable oils are transformed to derivatives, for example, alkyd-based polyols and alkyd resins. Then,

polyols are reacted with different diisocyanates to realize polyurethanes (PU) coatings. PUs are produced from vegetable oils gained from various seeds like cotton, castor, neem, rapeseed, palm, jatropha, soybean, and so on. Other bio-based resources also are accustomed prepare PU coatings alongside with vegetable oils. Main raw materials for the assembly of PUs is eagerly made by using these reactive sites. Upon hydrolysis, triglycerides of vegetable oils make different glycerols and fatty acids.

Fatty acids have a full of life task in manufacturing greener polymers thanks to the multifunctional nature and long chain of methylene groups. Former investigations described that the addition of fatty acids to the polymeric material gives greater characteristics like flexibility, low temperature, better handling, and improved degradation to polymers compared to the straightforward physical addition of fatty acids to polymers. Many aspects mark the characteristics of oil-based coatings, like the comparing of various unsaturated and saturated fatty acids, the amount of unsaturation, location, length of fatty acid chains, and stereochemistry of the double bonds in fatty acid chains. Chain lengths of fatty acids between 12 to 20 C-atoms are more communal, which might be either unsaturated (linoleic, oleic, ricinoleic acid, linolenic, etc.) or saturated (non-reactive aliphatic chains like palmitic acids, stearic, etc.), whereas double bonds in unsaturated fatty acids are placed at position 9, 12, and 15. The typical number of double bonds per each triglyceride varies in several oils. Fatty acids will be part of polyester polyols, while hydroxyl functional vegetable oils are straightly employed in PUs. Various plant-based PU coatings are manufactured from vegetable oils and other renewable resources together with their possible uses [13].

Moreover, flexible bond of ether/ hydrocarbon part causes flexibility in bio-based polyurethane resins. The important key in formulation of polyurethanes is that the ratio of hydroxyl (OH) to isocyanate groups (NCO). A moisture-cure room-temperature resin is obtained when the ratio of NCO/OH is larger than 1. Additionally, the handling and properties is adjusted by changing the formulation, structure, and reaction situations.

2.6 Acrylic

Acrylic polymers are used extensively within the coatings industry. Acrylic resins are essential to the coatings industry because of proper hardness, chemical resistance, and moisture resistance compare to the other polymers that may currently be synthesized from bio-based materials. Although the requirement for sustainable bio-based coatings is high, the industry is at home with the superb physical properties of petroleum-based coatings. It is unwilling to require a step back in performance. For these reasons, funding for research on high-performing, bio-based acrylics is critical to produce the advanced materials required to drive bio-based coatings implementation. Preliminary test data derived from experimental coatings using these new bio-based acrylics have shown them to be better at dispersing pigments in waterborne coatings than corresponding petroleum-based polymers. Since high-throughput methods are being

employed, the program will provide extensive data to totally understand the simplest bio-based materials and reaction conditions needed to get the simplest coating properties. A life cycle analysis is conducted on a model dispersion to make sure that the new material is helpful to the environment compared to a petroleum-based control. The proposed program's successful completion will provide a prototype polymer customized to deliver green bio-based coatings to finish markets as diverse as automotive primers, consumer electronics basecoats, and architectural house paints. The spread of those coatings into the market will provide a value-added marketplace for agricultural and forestry materials, reduce dependence on foreign oil, and conserve energy by utilizing energy-efficient production methods [14].

2.7 Lignin

Lignin is plentiful and versatile and has significant potential as a green energy producer. Though it is often apparent as having imperfect business occasions, Lignin is ideal for requests demanding a rigid building and may be mined from plant-based material to be used as a renewable, economic, nontoxic substitution to fossil-based raw materials, containing phenol in coatings. Many studies, comprising inventions, are obtainable within the research on lignin in paint and coating's requests. A Chinese report defines an ecologically preparation procedure of an economic inner wall coating [15]. Moreover, lignin is employed to formulate phenolic, polyester, polyurethane, and epoxy resins, consequently utilized. As an example, thanks to the attendance of the lignin structure within phenolic groups, this could substitute bisphenol-A to synthesize epoxy binder. Ferdosian et al. depolymerized organosolv lignin first by reductive depolymerization in supercritical acetone at 623 K at the atmosphere of 10 MPa H_2 within the presence of Ru/C catalyst [16]. The gained depolymerized organosolv lignin, with a high hydroxyl number occasional and average relative molecular weight, was wont to manufacture lignin-based epoxy prepolymers. At the perfect synthesis situations, that means, 8 h at 328 K with NaOH/DOL molar ratio of 6.3, a high epoxy content of about 8 and high product yield (99%) were accomplished. An invention in 2015 relates to polyester polymers prepared from lignin such the lignin is incorporated into the backbone of the polyester polymer [17]. The invention further relates to coatings comprising such polyester polymers and substrates to which such coatings are applied.

2.8 Shellac

Shellac could be a resin concealed by the feminine lac bug on trees in India and Thailand's forests. It is treated and sold as dry flakes and solved in alcohol to create liquid shellac utilized as a colorant varnish, wood coating, and food varnish. Shellac utilities as high gloss finish, sanding adhesive, rigid bio-primer, antiodor/stain, and

antitannin coating. Shellac-based varnishes could also be utilized on surfaces thanks to its brilliant insulation capabilities causes closing the introduction of moisture. This biopolymer is thermoplastic and offers high adhesion to the surfaces. Solving the shellac in ethanol/methanol produces a durable and hard coating. Additionally, shellac may be a UV-resistant bio-polymer since it does not darken because it is applied for a while. Shellac creates stiff, and glossy film with high adhesion to surface, hence it is significant in coatings and paint industries. Thanks to its weak chemical resistance properties, shellac has not perfect usage for industry. Though significant development in shellac coating properties like impact resistance, scratch hardness and gloss were detected on blending with epoxy novolac resin [18]. Acid resistance decreased while alkali and water resistance and increased, with increased amount of epoxidized novolac resin within the blends. Study of the contact angle measurement shown that blends showed less resistance towards non-polar than polar solvents ones. In studies, in a two-step polymerization method urea–formaldehyde (UF) resin-coated shellac resin microcapsules was manufactured [19]. The consequences of various amount of microcapsules on color difference, gloss, adhesion, hardness, and impact resistance of water base coating films were investigated. Simultaneously, the healing effect of the arranged microcapsules employed in water base coating film was debated. The final results discovered that the shellac resin microcapsules which are coated with urea–formaldehyde resin were fruitfully organized. At the 0.75:1 and 0.67:1 core–shell ratios, the color differences of the coating film with 0–20 wt.% microcapsules were negligible and also the color was shown to be uniform. A proper gloss was obtained under the condition of 60° incident angles at the same microcapsule concentration. At the concentration of 20 wt.%, the coating film hardness reached the most value. The coating film adhesion was improved, which was not littered with concentration of microcapsule. At the concentration of 5wt.% and 10wt.%, the paint film was shown to have an acceptable microstructure. The coating film with a 1wt.% concentration of the microcapsules of shellac resin coated with urea–formaldehyde resin was shown to have a better comprehensive performance and self-healing properties [20].

2.9 Rosin

Greek pitch or colophony may also have called rosin. It could be a solid form of resin made by heating fresh liquid resin vaporize the volatile liquid terpene derivatives gained from pines and a few other plants. It is semi-opaque with various colors from black to yellow. Rosin is brittle at room temperature, but it can be melted and liquefied at high temperatures. The most organic materials in rosin are unsaturated mono-basic acid, Abietic acid, and other kinds of acids. Rosin is usually utilized in coating industries. It is employed in low scale in vegetable oil or fillers that are utilized in construction products. Rosin can modify alkyd resins which made them desired in paints and coating industries thanks to better some properties, like gloss and hardness [21].

2.10 Pullulan

Pullulan is other reasonably natural polymer formed by particular *Aureobasidium pullulans*, polymorphic fungus strains, as a water soluble, extracellular polysaccharide. *Aureobasidium pullulan* could be a ubiquitous fungus established in natural materials like water and soil, mostly as an early-colonizing saprophyte on decaying wood, leaf litter, and plenty of other plants, within which they use cellobiose but not exactly the cellulose [22]. The distinctive design of the linkages of α -(1 \rightarrow 6) among the maltotriose subunits offers unique physical properties of pullulan, containing high structural flexibility and water solubility [23]. Subsequently, these characteristics provide the pullulan with physical traits, together with adhesive properties, and permit its compression capacity, thus molding strong, forming fibers, and oxygen-impermeable films [26]. Pullulan is insoluble in organic solvents, but extremely water-soluble, non-hygroscopic, and owns rather different relative viscosity than other polysaccharides, that is, moderately low as compared to most gums, especially the Arabian gum. Otherwise, pullulan-based bio-nano-composite coating materials are invented the primary time, combined with montmorillonite via the ultrasound-assisted technique for the exfoliation of inorganic tactoids. Accordingly, the coating material demonstrates an acceptable oxygen barrier [24].

2.11 Vegetable Oils

Vegetable oils are achieved from the seeds of the plants and existed in nearly all vegetable oils. They carry both unsaturated and saturated fatty acids and triglyceride esters of fatty acids. In step with the degree of unsaturation in oils, they are in three groups of drying, semi-drying, and nondrying oils [25]. Moreover, vegetable oils have different functionality, as an example Karanja oil is utilized as antimicrobial agent; cotton seed, soybean, safflower, canola, and sunflower oils are utilized in formulation of ink; and many oleo-chemicals like curing agents (fatty acid-based poly(amidoamine) or polyamine), surface-active agents, solvents (low volatility) are utilized in coatings. Vegetable oils like *Vernonia galamensis* and *Euphorbia lagascae* seed oils contain > 60wt.% of a vernolic fatty acid based epoxy) that may be considered as a reactive diluent for coating applications. Marigold or *calendula officinalis* oil like Tung oil contains more than 63% of calendic acid (a C18 conjugated triene fatty acid), which give them the film formation property. The chemical derivatives of these kinds of oils are valuable and mostly consider as film-former in emulsion systems. Likewise, aperient and *Lesquerella* oil enclose hydroxyl functional group bearing fatty acids and may be utilized to formulate different bio-based resins for paint industries. The chemical derivatives (Dimer acids/ Diels Alder), of polyunsaturated fatty acids/esters, are also favorable bio base oil components for coating applications. Dimer acids are non-crystalline liquid dibasic acids with moderately high mass that modified by isocyanate utilized within producing of polyester resins with acceptable coating properties [15].

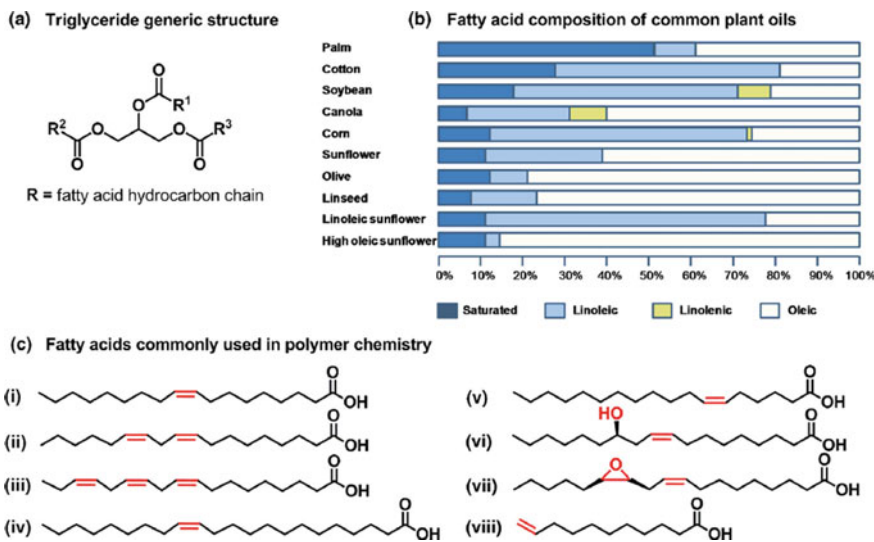


Fig. 3 a General triglyceride structure. b Fatty acid percentage composition of common plant oils. c Fatty acids commonly used in polymer chemistry: (i) oleic acid, (ii) linoleic acid, (iii) linolenic acid, (iv) erucic acid, (v) petroselinic acid, (vi) ricinoleic acid, (vii) vernolic acid, and (viii) 10-undecenoic acid. *Reproduced with permission from Elsevier [Materials Today 16 (2013) 337–343] [26]*

The main components of vegetable oils are triglycerides, which are obtained by esterification of glycerin with three fatty acids. The chemical structures of some fatty acids are shown in Fig. 3. These triglycerides contain several active sites, such as dual bands of stereo groups, which can form new structures.

3 Additives

New technologies enable the manufacturers to extract hemicellulose, sugars, and lignin from biomass enhanced and produce new, valuable products from these different fragments as additives in coating industries. In following part, bio-based additives has been reviewed.

3.1 Cellulose

Cellulose with the main unit of cellobiose could be a high relative molecular weight polymer with a linear structure [3]. Main considerable bases of cellulose are hemp pulp, wood, and cotton. Cellulose is crystalline with strong hydrogen bonding, high

relative molecular mass, and stiffness that made it un-permeable, so it is not soluble in common solvents and it is difficult to utilize straight in coatings. Therefore, hydroxyl groups in cellulose should be treated and transform its structure to corresponding acetal, ester, and ether derivatives. Most derivatives of cellulose, like hydroxyl ethyl/methyl propyl, methyl/ carboxyl methyl, and hydroxyl cellulose, are utilized as a film formers or rheology modifier and thickening agents in water base coatings and protective colloid in emulsion coatings. These derivatives may obtain in various forms of supported mass, dispersibility in water, and degree of substitution. Cellulose products may utilize in numerous applications like building additives and water-borne coatings. Non-cellulosic polysaccharide as an example a treated gum hydroxyl propyl gaur is additionally utilized in paint and coatings and brings more sag resistant and pseudo-plastic behavior than cellulose derivative-based products [27].

3.2 *Starch*

Starch as hydrocolloid bio-based polymer is extracted from plants and could be a polysaccharide designed by covalent bonds of the many glucose units. It is a branched/ amorphous amylopectin and linear crystalline amylose. This can be an economic polysaccharide, plentifully obtainable, and one in all the low-priced biodegradable polymers. For using starch as a thickening, gluing, or stiffening agent in coatings, it should be dissolved in warm water. Starch-based materials have the disadvantage of brittleness, water sensitivity, and relatively poor mechanical properties. To overcome these difficulties, it is treated by acetylation using pyridine and acetic acid [28]. Starch can be used as a modifier for fillers like kaolin via encapsulation of filler particles and realize noteworthy filler loading levels without accompanying strength losses [29]. It is established that a platy clay coating will yield the next raise in strength per unit weight of application as compared to a fine clay and more so if the clay is encapsulated in starch. Starch encapsulation of clay produces a more notable increase in strength than a similar weight proportion adding of starch to a kaolin formulation mixture. The measurements and observations of changes within the coated samples' various physical properties are clarified by a proportional loss of void volume within the coating from the process of encapsulation and therefore the increasing the stress transfer by presenting the higher surface to thickness ratio of the platelet [30].

3.3 *Protein*

Proteins which most of them are infusible and insoluble can be achieved both from plant and animal sources. Common proteins contain collagen, silk, and wool. Therefore, they will be utilized as reinforcing materials and it is hard to utilize them in coatings. Compared to synthetic polymers, the quite low cost of proteins, mostly plant proteins, is thus eye-catching for coatings.

3.4 Chitosan

Chitosan, a nitrogen-containing polysaccharide found from crustacean waste's exoskeleton (shell, head, and claw of sea organisms as crabs, shrimps, and lobsters) may be a deacetylated derivative of chitin. Chitosan is just soluble in a very few dilute acid solutions. The principal parts of chitosan structure are glucosamine units. It could be a linear polysaccharide formed of randomly distributed β -(1–4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). Chitosan has numerous possible biomedical and commercial usage. It is prepared by modifying crabs and other crustacean shells with hydroxide [31].

The self-healing coating will be arranged by utilizing chitosan-based coatings. In many research, chitosan was accustomed achieve as a healing material. Coating of the glass substrates with a chitosan modified polymeric binder in several quantities has been prepared. In another study, self-healing properties of chitosan in water base polyurethane as a sequence extender of PU pre-polymers were investigated [32]. Efficiency of self-healing and physical characteristics of waterborne PU were investigated by increasing the chitosan molar fractions of chitosan from 0.1 to 0.3. The efficiency of self-healing for the enduringness of the very best chitosan amount was established to be 47%. The scratch of the surface was also totally returned to its initial status. The sample's efficiency of the control sample without chitosan was 4% while that of the sample with minimum chitosan amount was found to be 35%. It is inferred that self-healing waterborne polyurethanes are often synthesized by chain extension with chitosan.

The usage of bio-based polymeric materials for eco-friendly corrosion inhibitors organizes a stunning and quite unknown method to developing green self-healing coatings. Chitosan is one such thrilling nominee thanks to its perfect adhesion to metallic surfaces and plenty of organic polymers, acceptable film-forming characteristics, and also the capability to make systems with potential corrosion inhibitors reversibly. In studies, a coating is made by a pre-layer based on chitosan deposited onto the metallic surface and a hybrid barrier film. The chitosan film doped with cerium ions functions as a reservoir for the corrosion inhibitor. The ions of cerium produce a metal complex with the chitosan functional groups, making a control release of the active material upon request. This kind of bi-layer protective coating was went to aluminum alloy 2024, widely utilized in the industry of aeronautical. The conclusion gained from electrochemical impedance spectroscopy reveal superior corrosion protection when the coating with the cerium-doped biopolymer pre-layer is utilized. The recent group evaluated chitosan functionalization with fluorinated substituents as a possible route to progress the barrier and surface properties of the coating matrix. The localized electrochemical investigation in micro-confined defects demonstrated a precious self-healing capability of the developed coating system [33].

It absolutely was seen that the layer of chitosan played as a reservoir for cationic Ce^{3+} corrosion inhibitor thanks to the complexation of Ce^{3+} with chitosan amino groups, which prevents its incontrollable and fast leaching. The corrosion tests

evidence the self-healing ability of prepared chitosan-based green protective coatings. The interaction between Ce^{3+} and chitosan and therefore the former's concentration end in the latter's performance from a corrosion standpoint is additionally discussed. Furthermore, these coatings were established to confer active corrosion protection toward aluminum alloy 2024, as shown by electrochemical impedance spectroscopy.

Antibacterial agents are one of the general additives in water base coating formulation. Using ecological materials in the formulations of coatings is strongly recommended by increasing environmental limits about toxic materials and additives. An exploration work presents using of chitosan biopolymer as an antibacterial biocompatible additive in cathodic electrodeposition bath. The electrocoating formulation was investigated as a function of chitosan amount. Different non-volatile contents of chitosan solutions were prepared in lactic acid and introduced to the formula. The final film properties and electrodeposition procedure were studied by Pierce film growth model and optical microscopy. The chitosan amount expressively affects the final electrodeposited films and of course the chitosan solution structure within the bath. The results demonstrate that 0.125% v/w concentration encompasses an appropriate antibacterial activity and makes a suitable electrodeposited film [34, 35].

4 Pigments

Pigments were achieved from animals, plants, and rocks and other natural sources. It was synthesized in 1856, Mauveine, which started the industries' applications of synthetic pigments. Though latest findings have demonstrated some synthetic pigments are carcinogen and that they have allergenic effects so, their usage in cosmetic, food, and pharmaceutical products is restricted or prohibited by the Food and Agriculture Organization of the world organization (FAO), the World Health Organization (WHO), and also the US Food and Drug Administration (FDA). The progressing of consumer knowledge has stimulated industries to use many natural pigments in recent years. Therefore, bio-based pigments or economic natural pigments have focused on recently. Natural pigments obtained from animals, plants, and microorganisms are mostly environmentally friendly, biodegradable, and biocompatible with low toxicity. The drawback of plant and animal usage for natural pigment is being unstable and high soluble, season dependent and has certain species' loss for large-scale production. Though biotechnological pigment production has more beneficial because of their higher growth rate, they are not full of seasonal differences and that they have high stability. A study showed that fungi are generally chosen for industrial-scale production of natural pigments among the microorganisms because bacteria are more exposed to environmental conditions and algae need sunlight.

Furthermore, the very best rate of growth of the marketplace for natural pigments is around 7% annually. Moreover, the fabrication of natural pigments in industrial scale should have a profitable procedure. The value of microbial bio-pigment manufacture

38–73% depends on the choice of raw materials. Consequently, the raw materials chosen within the manufacture of bio-pigments utilizing fungi should be both rich in nitrogen and carbon sources and good price to property ratio. Food or agricultural by-products created from industries that have newly increased important consideration thanks to their ability to achieving new treasured products with a zero-waste approach [36].

5 Solvents

The European project “Eco paint Bio-based formulations” (ECOBIOFOR), sponsored by 7th Framework Program of the eu Union, has dedicated on the progress of bio-solvents from renewable resources over biotechnological means and chemical procedures in line with the base of green chemistry. The goal is that the bio-solvents developed under the ECOBIOFOR project outline will substitute current petrochemical-based solvents, promoting a more ecological production and consumption by their use in organic coating industries. A multidisciplinary and complementary group was founded to attain these objectives. The necessity to substitute conventional petrochemical solvent utilized within the formulation of coatings, inks, adhesives, paints, and varnishes with “green” materials. ECOBIOFOR is, a project which contribute to a more sustainable way of manufacturing solvents from renewable resources, because it aimed to

- Develop novel sustainable chemical synthesis routes for commonly used solvents in coatings,
- Develop reactive solvents (which do not evaporate but are built into the coating) and,
- Validate these bio-based solvents in coatings.

The traditional petrochemical-based solvents result from oil refineries followed by some chemical steps. As an alternate route, ECOBIOFOR will build on:

- Use of renewable starting materials,
- Synthesis routes consistent with Green Chemistry,
- Biotechnological processes (enzymatic transformation),
- Paint -formulations with reduced VOC emissions.

A complete study of the feasibility of using renewable resources to synthesize bio-based solvents then produce coatings using them has been dole out. Two different approaches are developed.

The first strategy for synthesizing solvents was via chemical transformations of renewable starting material following green chemistry rules and simplified processes and methodologies. The second strategy for synthesizing reactive diluents was via enzymatic conversion of a molecule deriving from vegetable oil [37].

The consumption of bio solvent was mainly dedicated to cleaning operations and merely 0.63 Million Tons (12.6%). Though consumption of bio solvents has an ascending trend and boost annually, 4.8% up to 1.1 million by 2020 (EU Innova-Biochem 2010). The most usage of the solvents belongs to the adhesives, inks, and coatings industry which utilize 58% of the amount of solvent production because the chief constituent in their formulations (50–70 wt.%). The economic and environmental anxieties are strong. EU Directives put pressure on the companies to progress greener solutions, but until now, irrespective of this concern, only 1.5% of bio solvents are utilized in paints. So, the coatings sector pushed the requisite for brand spanning good and new bio solvents. ECOBIOFOR project objects to create solvents for coatings with three specifications: bio-based (coming from biocompatible resources), produced consistent with the standards of Green Chemistry, and new formulations with lower release of volatile organic content (VOC). Some of companies are dedicated to remodeling biomass to basic chemical products with established industrial uses [37].

6 Conclusions and Future Trends

Responsible manufacturers who are looking to scale back their ecological footprint from regulations requiring minimum bio-based content in finished products leads to the increasing emphasis on bio-based materials. Manufacturers also are looking to learn from government incentives on the utilization of bio-degradable resources. Formulating coatings with bio-based binders further reduces the coating's fossil content by using bio-based alternative instead of petrochemical-based resin.

Coatings manufacturers are continuously attempting to find cheaper ways of changing bio-products into the monomers needed to create raw materials. Numerous bio resins, pigments, additives, and solvents with appropriate formulations are utilized as eco-friendly materials for paint and coating's industry. Therefore, such bio-based components are the simplest option as raw materials for coatings. These attitudes have upgraded the sphere of applications and also the physicochemical properties and mechanical properties of bio-based coating films.

Moreover, progressing their functionality and achieving new styles of properties may be reached by high knowledge of bio-science and bio-technology. Consequently, sufficiently designed biomaterials with required variable features are considered for future within the coating industries. Moreover, the longer term viewpoint for evolving novel paint and coating with greater value is promising.

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