Chapter 2

Biodegradable Plastics from Renewable Raw Materials

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Abstract

Fossil oil prices are soaring steeply due to the depleting petroleum raw materials. Extensive research has been carried out around the globe to develop efficient processes that can replace oil-derived polymers (conventional plastic) with bio-based polymers that originate from renewable resources. Fossil-oil based plastic products take decades to degrade, leading to the unwanted accumulation of plastic waste that can be seen all around. Further, greenhouse gases emission occurs during the production and destruction of synthetic plastic. Therefore, plastic waste has become a massive threat to the biosphere and needs to be addressed immediately. To overcome this issue, a new type of plastic can be produced from bio-resources that can fulfill even the energy demand in today's world. This new form of plastic must be accommodated fast in daily life, considering the range of applications of plastics. Biodegradable plastics made from renewable raw materials can retain all the benefits of petroleum-based plastic without having any negative impacts on the environment. Bioplastics are not toxic in nature and can easily decay back into carbon dioxide via degradation. The products made from bioplastics may be commercialized, considering their superior properties over conventional plastic. The discovery and implementation of plastic made from renewable raw material resources could be a giant leap into the sustainable future.

Keywords

Bio-Degradable Plastics, Biopolymer, Bio-Based Polymers, Renewable Resources

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1. Introduction

Products made from plastic have been widely used by humankind on a daily basis, serving the non-lasting demands of our fast-paced lifestyle. Society demands a considerable amount of plastic for the manufacturing of millions of products. Though plastic has numerous advantages over conventional materials, it also poses a massive threat to the environment since the degradation period of plastic products can vary from 20 to 500 years. Despite the fact that plastic can be recycled and reused, the high cost of the process and the confined market for recycled products, deposition of solid waste of plastics can be seen all around. Nearly 300 million tons of plastic are produced worldwide every year [1]. The accumulation of synthetic plastic has been continuously rising around the globe and has emerged as a crucial environmental issue that needs to be addressed immediately. Moreover, the production of plastic also consumes a high proportion of oil, a non-renewable resource that is running out of supply. Most of the plastic originates from oil and is composed of synthetic polymers; however, polymer chains can also be obtained from natural resources.

The idea of having material derived from nature with environmental interests of being biobased and/or biodegradable is a lucrative choice to the consumer and industry. From an environmental point of view, natural renewable resources could be employed for the synthesis of plastic while producing plastic material that is biologically degradable at specific conditions of humidity and temperature [1]. On the one hand, it can reduce the consumption of a dwindling supply of fossil resources while reducing the emission of greenhouse gases, providing an eco-friendly alternative to the traditional plastic that can ultimately reduce the negative impact on the environment. Natural renewable resources could be a plant, animal, or microbial biomass that is being used for the production of material or energy apart from food and feed area [2]. Frequent use of natural renewable resources can also boost the field of forest and agriculture while leading to alterations in bio-based chemicals and materials. However, it is imperative that these renewable raw materials must be employed sustainably in a way that they set a minimum impact on the soil, water, air, and climate.

Since the last few decades, bioplastic has been recognized as an essential invention that serves the plastics and chemical industry by presenting numerous opportunities [3]. However, bio-based plastic only endures just over 1% of the total global plastic market, which is still a tiny fraction [4]. Nevertheless, the production of plastic has been rapidly replaced by bio-plastics such as polyethylene, polyhydroxyalkanoate, polylactic acid, etc [5]. Natural renewable resources can be employed in the production of biopolymers that comprise in large part, or even wholly, renewable resources. The biopolymers can be derived from various sources, including vegetable, animal, and microbial biomass/products. Vegetable origin can offer biopolymer synthesis from starch, cellulose, lignin, chitosan, pectin, zein, etc. In animals, whey protein, gelatin, and casein are the most popular sources; whereas, polyhydroxy-butyrate and polyhydroxy-valerate are widely popular in microbial origin [6,7]. Since its discovery, biopolymers have been an integral element of human development and served in the field of food, medical, packaging, food additives, and water treatment, among many others [8,9]. However, the emerging generation of biopolymers is still in its infant stage that needs several developments considering the demand for the environment-friendly alternative of synthetic plastic [10,11].

2. Types of bioplastics

Bioplastics can be a group of different materials; based on biodegradable ability, type of biomass used, or a combination of both (Fig. 1). For instance, there are forms of biobased materials that are not biodegradable and fossil-based materials that are biodegradable. Moreover, bioplastics can also be found in a multi-layered form blended with fossil-based plastics [12]. Bio-based plastics can be classified as novel or drop-in plastic. A few forms of bioplastics are completely novel materials such as polyethylene furanoate (PEF) and polylactic acid (PLA), unlike drop-in plastics that have a similar structure to their fossil-based counterparts [13]. Bioplastics can be further categorized based on their source and degradability. The following are the three categories of bio-plastics: a) bio-based, b) bio-degradable, and c) bio-based and bio-degradable.

2.1 Bio-based plastics

The bio-based plastics originate from natural renewable resources such as agriculture-based raw material, hemp, sugarcane, potatoes, corn starch, etc. These resources are abundant in nature and help to reduce the emission of CO₂ by replacing traditional plastic. Some examples include polyamide (PA), polyethylene terephthalate (PET), and polyethylene (PE) [5].

Fig. 1 Material coordinate system of bioplastics

Polyethylene

Polyethylene (PE) derived from natural renewable resources is flexible and brittle/rigid in nature, showing identical physical and chemical properties when compared to conventional polyethylene. Several agricultural feedstocks can be used in the synthesis of bio-based polyethylene, including corn, sugarcane, etc. It was also observed that the emission of CO₂/kg was far less when compared to the traditional form of polyethylene [14]. Biobased PE can serve a similar purpose by exhibiting similar properties as the conventional form. Additionally, bio-based PE has demonstrated better durability that makes it an obvious choice over conventional PE [5,15].

Polyamide

Vegetable oil is a source to derive another form of bioplastic, polyamide (PA). Castor beans have proved an efficient source for the production of PA; however, it lacks biodegradability. Biobased PA has shown several better features when compared to conventional PA, such as low cost, superior appearance with better dimensional stability while providing superior water, chemical, and thermal resistance. Moreover, it also records a little environmental impact over conventional form. Bio-based PA is mainly being employed in packaging, automobile, and electrical industries, where durability, safety, and versatility are significant concerns for manufacturers [5,16].

2.2 Bio-degradable plastics

Bio-degradable plastic is a structure that originates from traditional raw materials and can be wholly degraded in the environment without employing any additional additives. This is mostly used as a one-time packaging material that can be disposed of after its use. It may take degradation time ranging from a few days to months, depending on the environmental conditions. Polycaprolactone (PCL) and poly-butyrate adipate-terephthalate (PBAT) are among many of these types of bioplastics available in the market [5,14].

Polycaprolactone (PCL)

Despite originating from crude oil, a few forms of plastic still show biodegradability. PCL is one such type that is not derived from a renewable resource and still demonstrates several attractive properties such as superior oil, water, and solvent resistance. It also has a lower melting point ranging between 58-60°C. PCL is mostly used for shorter life applications, and its lower melting point makes it easily amiable to composting as a means of disposal with a low degradation period [5,17].

2.3 Bio-based and bio-degradable plastics

A bioplastic that possesses properties of both bio-based and biodegradable plastics can also be used as an efficient means of biobased polymers. Polyhydroxylalkanoate (PHA) and poly lactic acid (PLA) are among many types of these plastics.

Poly lactic acid

Poly lactic acid (PLA) is a bio-based polymer mainly derived from agricultural resources (tapioca roots, potato, sugar cane, chips, etc.) and can be biologically degraded in the environment. PLA is the second most consumable plastic in the modern age due to its easy degradability feature that makes it an excellent candidate, considering the unfavorable impact of traditional plastic on the environment. Moreover, it has reduced carbon footprints, where it only produces 1.8 kg CO₂ compared to traditional plastic (6 kg). PLA is mostly used in products meant for longer period usage [5,13].

Polyhydroxylalkanoates

Polyhydroxylalkanoates (PHA) is another type of plastic that exhibits properties of both bio-based and bio-degradable plastic. It is a UV stable linear polyester generated by fermentation of sugar and lipids using bacterial strains. Agricultural raw materials are mainly used during the production of PHA using conventional processing tools. The bio-compostable and mechanical properties of PHA can be altered by blending it with other types of plastics, consequently widening its domain of application [5,16].

3. Advantages of bio-plastics

Bio-plastics have emerged as a promising alternative to petroleum-based plastics due to its remarkable features that favor numerous industrial applications. Global awareness concerning global warming that transpired due to severe pollution has led consumers and industries to reconsider their choices. Bioplastic is an obvious choice since it outperforms traditional plastics in several areas. Several features of bioplastics are as following; (1) Unlimited raw material: agricultural raw materials are abundant in nature and can be obtained on a yearly basis. Unlike the limited supply of fossil oil, natural renewable resources can be used for the production of plastic without worrying about its depletion, (2) Bio-degradable: bio-based polymers require less time to get entirely degraded after being discharged as waste (Fig. 2). Therefore, it does not demand any recycling, leading to less or no requirement of landfilling when compared to conventional plastic, (3) Requires less energy for production: the production process of bioplastic demands less than half of the energy when compared to the conventional form of plastics, (4) Reduces dependency on foreign oil: It also reduces the import of fossil oil that is the primary raw material for the production of conventional plastic, (5) Non-toxic in nature: since conventional plastic is composed of several harmful chemicals [18] and it releases several toxic gases during its breakdown, making it harmful to the environment. On the contrary, bioplastics are entirely safe and do not require or produce hazardous chemicals/gases during their synthesis/break down, and (6) Bio-plastic is eco-friendly in nature: there are very few greenhouse gases, and less carbon emission generated during the production and incineration process of bio-plastics. Table 1 [19-59] depicts the different renewable sources for bioplastic production along with their respective applications.

Fig. 2 Degradation process of bio-based polymers

Table 1 *Different renewable sources for bioplastic production and their respective applications [19-59].*

Sr. No.	Source material	Material	Techniques	Properties	Applications	Ref.
1.	Potato peels, banana peels, cassava, wheat, Maize	Starch	Polymerization, casting,	Short-living, biodegradable and Compostable	Food packaging, medical devices, agriculture foils, textiles, automotive and transport, building and construction	[19–22]
2.	Bunch, citrus waste, corn leaf, oil palm fruit, rice straw	Cellulose	Polymerization, casting	Biodegradable, limited compostable,	Car interiors, construction materials, toys, medical applications, sports equipment, decor materials, etc	[23–26]
3.	Plant sources: Rapeseed oil, mesocarp fiber, corn; Animal sources	Protein	Injection moulding, casting	Biodegradable	Toys, sports gear, containers, packaging materials	[27–29]
4.	Wood, straws	Lignin	Injection moulding, plasticizer	Biodegradable		[30,31]
5.	Fungi, yeast	Chitin	Casting, moulding	Biodegradable, bio compostable	Thermoplastic material, Biomedical applications, packaging materials	[32]
6.	Shrimp, crab, mushrooms	Chitosan	Casting, moulding	Biodegradable, bio compostable	Biomedical applications, packaging materials	[33]
7.	Prokaryotic organisms	Polyhydroxy-alkanoates (PHA)	Fermentation, casting, evaporation.	Long-living, depending on composition fast biodegradable to non-biodegradable, limited compostable	Coating, food packaging, medical implant	[34,35]

8.	Lactic acid, paper waste, commercial polylactic acid	Polylactic acid (PLA)	Casting	Weatherproof, biodegradable, not compostable	Films, food packaging	[36–38]
9.	Bio-MEG, bagasse, hay, and sugar cane molasses	Polyethylene terephthalate (PET)	Polycondensation	Long-living, biodegradable	Soda and drinking water bottles, automotive interiors, packaged goods, electronics and construction goods,	[31,39]
10.	Bio-MEG and 2,5-furan dicarboxylic acid (FDCA) from lignocellulose biomass	Polyethylene furanoate (PEF)	Polycondensation	Non-biodegradable and non-compostable	Packaging industry for milk, soft drink, water, and alcoholic beverages	[31,40]
11.	1,3-Propanediol from glycerol, vegetable oil	Polytrimethyl terephthalate (PTT)	Polycondensation	Non-biodegradable and Non-compostable	Fiber manufacturing, textiles, and carpet synthesis	[31,41,42]
12.	Carboxylic acid from lignocellulose,	Alkyds Resin	Polycondensation	Biodegradable, biocompatible	Paints, lacquers, production of printing inks, adhesives, insulating	[43,44]
13.	Butanediol and succinic acids from starch	Polysuccinate	Polycondensation	Biodegradable, biocompatible	Fiber spinning, film blowing, and thermoforming	[45,46]
14.	Butanediol from starch, vegetable oil	Polyesters	Polycondensation	Biodegradable, biocompatible	Adhesives, casting material, insulating materials, and printing inks	[47–49]
15.	Castor oil	Polyamides	Step-growth polymerization	Depending on composition, biodegradable to non-biodegradable	pneumatic air brake tubes, flexible oil and gas pipes, electrical cable jackets, and automotive fuel lines	[50–52]
16.	Plant oils such as soya or castor oil, vegetable oils	Polyurethane	Polycondensation	Biodegradable	Cushions, coatings, and insulations	[53,54]

17	Glycerol, fatty acids, or sugar	Polyacrylates	Polymerization	Non-biodegradable	Thickener, pigment dispersants	[55,56]
18	Sugarcane, vegetable oil	Polyolefins	Polymerization, cracking	Depending on composition fast biodegradable to non-biodegradable	Bags, pouches, petrol canisters, barrels, packaging, textiles	[57,58]
19	Vinyl chloride, ethylene from fermentation	Polyvinyl Chloride	Casting	Non-biodegradable and non-compostable	Wires, films, cables, pipes, and bottles	[17,58]
20	Vegetable oil, lignin, rosin, furan, sugars	Epoxy Resins	Ring-opening polymerization	Biodegradable	Adhesives, coatings, aerospace, and electronics industry.	[59]

4. Overview of renewable raw materials

Manufacturing of materials, chemicals, and other bio-based products at an industrial scale using renewable raw materials as a feedstock has gained attention since it helps to conserve fossil resources while making the process environmentally friendly. In comparison to the products based on fossil resources, bio-based products have shown excellent greenhouse gas balance over the complete life cycle and have less toxicity while requiring less energy for production as well as for disposal. A limited supply of fossil resources has driven innovation for the use of renewable raw materials as resources. A wide range of renewable raw materials, basically plant-based raw material, can be used for the synthesis of bio-based plastics. These raw materials can be classified as first, second, and third-generation feedstocks. All these resources can be procured, modified, and processed to obtain bio-based plastics. Today, biobased plastics are mainly synthesized from starch, sugar, plant oil belonging to the first-generation feedstock. In recent years, due to the reasonable competition with food and animal feed, lignocellulose feedstock has gathered significant attention towards its utilization to produce fermentable sugar.

First-generation feedstock

The first-generation feedstock includes carbohydrate abundant-plants such as sugarcane or corn that are suitable for human as well as animal consumptions. They are the most

efficient feedstock to produce bioplastic since their cultivation needs less land and provides a high amount of yields. The efficiency can be measured based on the annual yield of carbohydrates per hectare and the area (land) used per ton of bioplastics produced. The first-generation feedstocks include crops such as sugarcane, wheat, corn, potato, sugar beet, plant oil, rice, etc.

Second generation feedstock

The plant and crops that are not suitable for animal consumption (feed) and human consumption (food) are considered second-generation feedstocks. They can be non-food crops (cellulose feedstock, chitin, etc.) or waste material from first-generation feedstocks (e.g., waste vegetable oil). Lignocellulose biomass comprising a composition of cellulose hemicellulose and lignin are the most used second-generation feedstock. Lignocellulose biomass includes short -rotation coppice such as willow, miscanthus, poplar, or agricultural waste (by-products). Additionally, by-products from the forest or other biomass waste containing sugar and starch such as corncobs, bagasse, wheat straw, palm fruit bunches, and switchgrass are some of the examples of second-generation feedstock.

Third generation feedstock

Algae-based biomass is considered a third-generation feedstock for bioplastic synthesis. Algae biopolymers were mainly evolved as by-products of algae biofuel production. Algae can be more efficient while obtaining a higher yield of bioplastics when compared to first and second-generation feedstocks and does not require the use of pesticides, herbicides, fertilizer, or land to grow. However, the processing of bioplastic production is comparatively expensive and is still in its infant stage. Algae produce a variety of base materials such as carbohydrates, proteins, and hydrocarbons that can be used in bioplastic synthesis [60]. Different types of bio-plastics prepared by algae feedstock are as following: (1) Hybrid plastics: usually made by the addition of denatured algae biomass to petroleum-based plastics like polyethylene and polyurethane as fillers. Green algae are found to best suit as the hybrid plastic source. (2) Polylactic acid: bacterial fermentation of algae yields lactic acid, a biobased monomer that polymerized to polylactic acid. (3) Polyethylene: fermentation of algae with yeast gives ethanol, which can be further converted to ethylene, a biobased monomer that can be employed in the production of various plastic likes polyethylene. (4) Cellulose-based plastics: after the extraction of algal oil, 30% of algal biomass is left with cellulose, a natural polymer. This type of biomass can be useful for the production of cellulose-based bioplastics.

5. Production of biobased polymers

Production of bio-based and biodegradable plastics can be grouped according to their source (Fig. 3): (1) Polymers from biomass (agro-resources and agro-polymers) such as starch or lignocellulose, (2) Bioplastic polymers derived employing microbial fermentation such as polyhydroxyalkanoates (PHAs), (3) Bioplastic monomers derived using biotechnology approach comprising conventional synthesis, and (4) Bioplastic from industry-originated wastes.

Fig. 3 Classification of the sources producing biodegradable polymers

5.1 From biomass (by extraction and separation)

Polysaccharides and proteins are the main agro-polymers that can be used as a raw material for bioplastic synthesis. Several conventional techniques can be employed to process such types of biomass.

5.1.1 Polysaccharides

Polysaccharides are macromolecules comprising most of the biosphere. They are mostly found in structures of cellulose, carrageenan, chitin, pectin, etc., forming the main structural elements of animals and plants exoskeleton. They are composed of complex carbohydrates constituting glycosidic bonds. Among many, this chapter focuses on starch, lignocellulosic material, natural rubber, and thermoplastic elastomers.

Starch

Native starch

Starch is the central reserve for polysaccharides, a source of energy in plants. Starch is mainly stocked in seeds or roots of the plants and derived primarily in the form of cereals and tubers (e.g., rice, corn, wheat, manioc, potatoes, etc.) [27,61]. Starch, in its natural form, is composed of crystalline granules and cannot be soluble in water. Starch granules vary in size from 0.5 to 175 μm with various shapes such as polygon, sphere, platelet, etc., depending on their botanical source [62]. These are constituted of two homopolymers of α -D-glucose, amylose, and amylopectin. Amylose is a linear polymer, whereas amylopectin is ramified in nature. Although amylose is a minor component covering only 20-30 % in overall mass [63], its linear nature yields better flowing properties that make amylose-rich starch material, an excellent candidate for bioplastic synthesis [64,65].

Thermoplastic starch

The natural form of starch, chains exhibiting various intermolecular hydrogen bonds, lead to higher melting temperature (T_m) than its degradation temperature [66,67]. Therefore, to obtain plastic-like properties, it is essential to render high water content or/and some non-volatile plasticizers such as sorbitol, glycerol, etc., that help decreases the T_m [68,69]. This plasticized form of starch is known as thermoplastic starch (TPS). To fabricate TPS, the granular structure of starch has to be de-structured. Starch granules can be disrupted by employing the solvent-casting or melting process where starch is blended with plasticizers under the extrusion process (thermo-mechanical treatment) [27,70]. Starch plastification has gained considerable attention from researchers around the globe and is an extensively studied phenomenon [21,22]. The TPS can be obtained by employing a melting process that is often performed using plasticizers to get a homogeneous molten phase. The mechanism of the extrusion (a thermo-mechanical process) is widely studied (Fig. 4) [71], and several related factors can affect the overall water absorption capacity and starch solubility. It can also get highly influenced by several other experimental factors such as pressure, shear, humidity, and temperature [61]. Moreover, it gets affected by the viscosity of the chemicals and amylose/amylopectin ratio [72]. TPS offers desired

flowing properties close to the conventional form of thermoplastics originated from petroleum oils such as polyethylene (PE) or polypropylene (PP) [61]. These TPSs are widely being used as a matrix or as co-constituent blended with other forms of thermoplastics, to obtain several commercialized biodegradable plastics such as Biotec®, Novon®, and Mater-Bi® [73]. It can further apply in several biodegradable compositions, including films, injection grades, films, expanded materials, compression grades, etc.

Fig. 4 Schematic representation of the starch extrusion process

5.1.2 Ligno-cellulose material

Cellulose-based plastics

Cellulose is the most abundant polysaccharide found in nature that is a primary component of cell walls in higher plants. Around 1.3 billion tons of cellulose is obtained around the globe for numerous technical applications. Cellulose is an unbranched multi-sugar molecule that contains 100-1000 glucose molecules or cellobiose units. The cellulose molecule mainly binds to higher structures that support tear-resistant fibers in plants [31]. The cellulose content varies according to the botanical source of the plant. Hardwood contains 40-75% cellulose, whereas softwood contains 30-50%. In cotton wool, the content of cellulose can reach up to 95%. Several processes have been employed to obtain a robust form of biodegradable materials. A group of researchers has produced bioplastic from the cellulose-rich waste of rice, rice straw. A particular type of industrial extractor called Naviglio was used to pre-treat rice straw that was further treated with trifluoroacetic acid (TFA). TFA is capable of solubilizing cellulose with other organic matter in rice straws and forms a bioplastic material [75]. In another study,

corn leaf biomass was heated at high temperatures (150°C) and further treated with acetic acid and sodium chlorite (NaClO_2) solution to obtain nano-coating biomaterial that can be used in biopolymers [76]. A group reported biofilm production from milled orange waste by employing a casting method where the gelling ability of pectin associated with cellulosic fibers was found to be significant on the biofilm production [25]. Similarly, cellulose-based bioplastics from oil palm empty fruit bunch have been reported where obtained cellulose with cassava starch matrix was blended with glycerol as plasticizer [23].

Cellulose-based materials are mainly classified in two distinct forms: cellulose regenerates and derivatives. Cellulose in dissolved form using chemicals to restructure into film or fibers are known as cellulose regenerates. This cellulose regenerates are used to make several groups of textile materials such as artificial silk, viscose silk, and many others. However, only cellulose derivatives are being used for the production of bioplastic. Cellulose derivatives are mainly classified into cellulose ethers and esters [31]. When compared, cellulose esters are significantly more important for plastic manufactures. Cellulose derivatives can be obtained via the esterification of cellulose using organic acids [77]. Researchers made celluloid, the first thermoplastic material, by blending camphor (25 %) and cellulose nitrate 75 % (synthesized using cellulose and nitric acid) [78]. From a technical point of view, the most significant forms of cellulose esters are cellulose propionate (CP combined with propionic acid), cellulose acetate (CA combined with acetic acid), and cellulose butyrate (CB combined with botanic acid). Cellulose-based plastics are widely used in car interiors, construction materials, toys, medical applications, sports equipment, decor materials, etc.

Lignin based plastics

Changing the chemical and physical properties of lignin polymer is conceivable via several modifications. Advanced research in lignin has led to a new generation of lignin-rich plastics featuring superior properties to conventional plastic polystyrene and PMMA (polymethyl methacrylate). The innovative structure offering promising tensile strength can accommodate more than 80% lignin comprehending lignin sulfonate in the methylated or non-methylated form [79]. Moreover, the blending of these materials with plasticizers or other polymers can further improve their mechanical properties. Also, lignin can be used as a blending companion for several conventional plastics and natural fiber-reinforced plastics. Liquid wood is the most popular lignin-based bioplastic in the market that can be easily processed in injection moulding machines [31]. The strength of the liquid wood can be enhanced by blending with flax and hemp (natural fibers). Further, advanced thermosets are being formulated, employing lignin for epoxy, polyurethane, and phenolic resins.

Wood-plastic composites

Wood-plastic composites (WPC) are a special type of natural fiber-reinforced polymer (NFRP) that is manufactured by blending plastic and additives with wooden raw material. WPCs are thermoplastic processible compounds and can be processed by employing extrusion and press or injection moulding [2]. WPC's 3-D plasticity and greater stiffness, unlike its counterparts from conventional plastics, making it a favorable candidate. Typically, WPCs are used in handrails, fences, noise protection walls, harbor docks, etc. Newly developed WPC material comprising polyvinyl chloride and wood fibers in the ratio of 1:1 is used for the manufacturing of door/window frames, indoor furniture, and construction material [2].

5.1.3 Other material

Chitosan/Chitin

After cellulose, chitin is the second most abundant agro-originated polymer and can be found in the exoskeleton of fungi or arthropods, conferring crystalline microfibrils to the cell wall [32]. Similar to cellulose, whisker-shaped nanofillers can be obtained by acidic treatment of the semi-crystalline structure of chitin microfibrils and can be further combined into polymer form to develop nano-hybrid materials. Chitosan can be derived from chitin employing the deacetylation process. Amino groups of chitosan offer some specific properties when compared to chitin. When chitosan is exposed to the acidic treatment, amino groups get protonated, which makes it a water-soluble polycation. Carrageenan is one such polysaccharide that shows polyelectrolyte function; however, polyanions are widely produced from these agro-polymers [80]. Glycerol is among many plasticizers that can be blended with chitosan to obtain thermoplastic material similar to plasticized starch [81].

Natural rubber and thermoplastic elastomers

Rubber can be found in the form of caoutchouc, natural latex, and elastomers; that possess a common relation to plastics. Though synthetic rubber has been demanded by most of the world, 40% of the market is accommodated by caoutchouc [31]. Caoutchouc is a plant-based polymer that is a type of latex, which has a primary role in protecting the wound from bacterial contamination. However, by making deliberate slits in cultivated plantations, crude rubber can be obtained that can be furthered hardened by employing vulcanization. Similar to natural rubber, thermoplastic elastomers (TPE) are biological materials that can be used in plastic manufacturing. TPE has better elasticity and is not cross-linked in natural form, making it favorable for re-melting and can be used as thermoplastics. They can be found in both complete and partial biobased forms.

Thermoplastic polyurethanes (TPE-U) is one such candidate that is being widely used in several industries, including the shoe and tooth-brush industry, where hard-soft bonded properties are mainly required to produce desirable products. Similarly, thermoplastic ether-ester elastomer (TPC- ET) is produced in a hard-soft form, where petrochemical polybutylene terephthalate (PBT) extends hardening whereas polyether from 1,3 propanediol extends softening. These blends are mainly used for the synthesis of airbags in the automobile industry. Moreover, a complete bio-based TPE derived from bio-based polyamide 11 and polyether was reported in the form of polyether block amide that was used in the manufacturing of ski boots [31].

6. Proteins

Proteins are agro-polymers and crucial renewable resources produced by plants, animals, and micro-organisms. Though several proteins have been reported for the production of biodegradable polymers, only a few made it to actual industrial-scale production due to the high production and downstream processing cost. Plant proteins derived from soybean, corn (zein), wheat (gluten) are extensively studied. Proteins, including casein, collagen, or gelatin, and keratin, are among many well-established animal proteins. Similarly, fumarase, chymotrypsin, and lactate dehydrogenase are commonly used as bacterial proteins in bioplastic synthesis [27].

6.1 Plant protein

Soybean

Soybean proteins were the first agro-biopolymers that were extensively researched and used in the manufacturing of moulded materials. During 1930-40, it was being used in the manufacturing of parts of automobile industries where a substance composed of phenol-formaldehyde/soybean flour mixture was used [29]. However, it was discontinued due to the comparatively lower costs of synthetic plastics. Soya proteins are still being used in the manufacturing of bioplastic due to the demand for biodegradable products. Typically, a dried soya bean contains crude protein (38-42 %), carbohydrates (33 %), and triglycerides (16-20 %) [27]. The soya proteins can be processed via physical or chemical treatments. For polymer processing, several processes can be employed, such as casting, designing, extraction, injection moulding, etc. Reports suggest that the soya proteins blended with starch can favor the superior synthesis of bioplastic products such as toys, sports gear, containers, packaging materials, etc. Plastic obtained through injection moulding has shown superior water-resistant properties while making these products easy to recycle and reuse. Similarly, films can be obtained using soy proteins that can be used as UV protective material making them applicable in packaging material. They can also

be used for land fillings since they quickly degrade in the environment. If processed properly, soy proteins can also be used to obtain foam products as well as insulating materials having superior thermal properties. Moreover, non-electrostatics, non-flammability, and efficient biodegradability make it an excellent candidate for the bioplastic industry.

Corn (Zein)

Corn accommodates about 9% protein and is mainly composed of zein, albumins, glutelin, and globulins. Zein is a highly hydrophobic protein that is soluble in alcohol [82]. It is typically extracted from corn employing the wet-milling process [83]. It is a by-product of ethanol production. Zein's hydrophobic properties make it water-resistant, a desirable characteristic in bioplastic production. Moreover, it is entirely biodegradable and also contains amino acids that are rich in nitrogen; therefore, it can be used as a fertilizer in agriculture after being used since it supports and promotes plant growth [84].

Wheat (Gluten)

Gluten, a wheat protein, has successfully attracted researchers from the bioplastic field during the last few decades, and a few materials produced from wheat proteins have been reported as well [85]. Typically, the processing of protein-based material requires the following steps: 1. breaking of intermolecular bonds using chemical or physical rupturing agents that stabilize polymers. 2. Rearrangement or re-orientation of polymer chains in the desired size and shape. 3. Lastly, allowing the formation of intermolecular bonds that maintains the 3-D network [86]. This can be attained using the casting method or physio-chemical method via employing chemical reactants in the process. A group of researchers has successfully prepared bioplastic from wheat gluten by using a casting method while employing plasticizers in the process [28]. Some specific applications of wheat protein-based products are developed by manufacturers of toys, office products, leather imitation, design, and furniture, etc.

6.2 Animal protein

Casein

Casein is an animal protein that can be used for the production of bioplastics. It is usually found in mammalian milk, such as cow milk (making 80 % of total protein content) and human milk (making 60-65 % of total protein content) [61]. Casein is an open and random coil structure of predominant phosphoprotein. Acid-precipitation can be used to obtain caseinates casein with an alkali solution. It can be found in various forms such as insoluble casein, particle calcium salts, or entirely soluble sodium or potassium caseinates [87]. Both caseins and caseinates can be used to obtain aqueous solutions that

can further be applied to produce transparent films without treating hydrogen bonds [88]. Similarly, to build a casein-based plastic, plasticized casein from skimmed milk can be treated with formaldehyde to obtain a cross-linked plastic followed by the removal of water. Casein-based plastic can be used in several areas to produce flower pots [61], where lignin can be blended with the products to increase their strength and stiffness. Furthermore, caseinates can be polymerized by gamma radiations by the creation of bityrosine covalent bonds [89] and employed in the production of biobased materials. However, due to its slightly substandard properties compared to the competitors, casein plastics are only being used in small niche markets [31].

Gelatine or Collagen

Gelatin is an animal protein derived from collagen. Collagen is elongated fibrils often located in fibrous tissues such as the cornea, blood vessels, bones, cartilage, skin, tendon and ligaments, and intervertebral disc. It is primarily used as a building material for capsules/tablets in the pharmaceutical industry. Moreover, it is also used as a nutritional supplement. Gelatin-based biofilms can be fabricated by solution casting method, and several products have been developed in the last few years. The production of bioplastics from a rapeseed meal by using injection moulding was investigated at varying mould temperatures [90].

7. From micro-organisms (fermentation)

7.1 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are aliphatic polyesters obtained via bacterial (sometimes yeast or plants) fermentation processes of lipids and sugars. PHAs can potentially replace traditional polymers (hydrocarbon-based) and are considered to be 100% bio-based and biodegradable in a varied range of environments, whether it is fresh/seawater or home/industrial composters [13]. PHAs can combine >150 monomers while producing a material with specific desirable properties of bioplastic. Moreover, they can alter the biological/mechanical compatibility employing enzymes while blending PHA with other polymers or inorganic materials, leading to a wide range of applications. Several bacterial strains can utilize sucrose, vegetable oils, glucose, glycerin, etc., as a source of carbon and energy where cells are exposed to the stressed conditions to make them produce PHA by expressing secondary metabolites. PHAs are a family of assorted plastics such as polyhydroxy-valerate (PHV), polyhydroxybutyrate (PHB), polyhydroxybutyrate-polyhydroxyvalerate (PHBV), and polyhydroxyhexanoate (PHH). Among several types of PHAs, PHB is a potential candidate to replace conventional polypropylene (PP) and polyethylene terephthalate (PET) due to its similar barrier, thermal, and mechanical

properties. PHB from the component of the bacterium *Bacillus megaterium* was reported in 1923. During the 1990s PHA has emerged as a potential candidate and received extensive attention around the globe; however, due to high processing cost when compared to oil-based plastic, it could not cover the anticipated portion of the overall plastic market.

A range of bacterial strains has been reported for the accumulation of PHA that comprises 30-80% of total dry cell biomass [91,92]. Bacteria are allowed to grow in a suitable medium provided with an adequate amount of nutrients so that they divide and grow at a fast pace. Further, they are supplied with excess carbon along with limited essential growth nutrients (deficiency of certain micro-elements: phosphorus, nitrogen, elements in traces, or lack of oxygen), encouraging them to synthesize PHA [93]. To isolate and purify PHA produced during the fermentation process, cells are concentrated, followed by drying. Further, the extraction of PHA can be carried out using solvents (chloroform/acetone). The solid-liquid separation process can be exercised to remove residual cell debris from the solvent containing PHA extract. Finally, the PHA extract can be precipitated using methanol and recovered by the precipitation process [94].

PHA synthesis in the soil environment can be beneficial due to the lack of phosphorus or nitrogen. The types of monomers and co-polymers produced are directly influenced by the type of carbon substrate supplied and the metabolism of microorganisms [35]. The most common substrates for PHA are fatty acids and glucose [95] that can be obtained from a wide range of agro-based biomass. Sugarcane and corn (glucose source) along with soybean and rapeseed oil (fatty acid source) are among some common raw materials that can be fermented by bacterial strains for PHA synthesis. PHAs are biocompatible and biodegradable, making them the right candidate for several industries. The non-toxic nature of PHAs favors medicinal applications where the implants need not be removed later. Similarly, PHAs can be used in the packaging industry for coating purposes as well as in consumer/household products. PHA growth has been increasing in the past few years; however, it is expected to grow steadily in the coming years. Researchers are also trying to produce the production of PHA from methane in low gravity environments. If it works, it could substantially push the growth for the PHA industry due to the abundant availability of methane[13].

From biotechnology (by conventional synthesis from bio-derived monomers)

The molecules that can be polymerized to obtain polymers and are derived from several renewable resources are called bio-monomers. These bio-monomers are polymerized to synthesize various types of bioplastics (e.g., polyesters, polyamide, polyurethane, polyacrylates, etc.).

7.2 Biobased polyesters (PLA, PET, PEF, PTT)

Polylactic acid

Polylactic acid or polylactide (PLA) is one of the most critical bioplastics in the market due to its abundant availability and relatively low price in comparison to other bioplastics [96]. PLA consists of natural acid, i.e., lactic acid obtained from various renewable resources such as corn starch, tapioca roots, and sugarcane, etc. [97]. Lactic acid is a chiral molecule with two different stereoisomers, i.e., L and D-lactic acid, and prepared by either chemical or biological methods [98]. The fermentation of carbohydrates produces lactic acid with the help of microorganisms such as lactic bacteria belonging to the genus *Lactobacillus*, or a few strains of fungi [97,99]. The process requires carbon sources such as carbohydrates, nitrogen sources such as yeast extracts or peptides and minerals element for the growth of bacteria while producing lactic acid. The polycondensation of lactic acid generally leads to the formation of low molecular weight polylactic acid. However, Moon et al. [100,101] have proposed an enhanced melt-polycondensation method using Sn (II) catalyst for the synthesis of high molecular weight. At present, ~30% lactic acid is only used for PLA synthesis, while the consumption of PLA is about 200,000 tons/year, thus presents a high potential for development [98]. The properties of PLA depend on their molecular characteristics and ordered structures such as crystallinity, morphology, degree of chain orientation, and spherulite size. PLA plastics have the advantage of film transparency, high rigidity, good thermoplasticity, and excellent processing performance on existing equipment [31]. However, PLA has a low softening temperature around 60°C, which limits its applications at higher temperatures [102]. The processed PLA is not a final plastic product; however, it can be used as a raw polymer for the specific application by copolymerization or compounding with suitable additives and can be further blended with other bioplastics. PLA can be plasticized by using citrate esters [103], low molecular weight polyethylene glycol [104], or lactic acid [105]. Using proper combinations of L- and D- lactides and additives, an enhanced version of modified PLA can be produced. This modified PLA can withstand high-temperature [37]. In comparison to polystyrene, PLA has a medium level of water and oxygen permeability and makes it suitable for different packaging applications [106,107]. PLA and PLA-blends are available in various grades and granulate forms that can be used for the manufacturing of drink containers, cups, film, moulded parts, bottles, and other everyday items [108,109]. Owing to their short life, the PLA has great potential for the manufacturing of items such as packaging films [38]. PLA can also be used in the manufacturing of desktop accessories, a casing of mobile phones, lipstick tubes, dashboards, door tread plates, and in textile applications depending on the fibers spun from PLA [37,39,110].

Polyethylene terephthalate

Polyethylene terephthalate (PET) is a thermoplastic polymer and one of the mass-produced plastic since the second half of the 20th century due to its extensive use in beverage bottle manufacturing. PET is generally produced by polycondensation of terephthalic acid/dimethyl terephthalate, and monoethylene glycol (or ethylene glycol, a diol or bivalent alcohol) having 70:30 composition ratio by weight [36,111]. Both the raw materials can be produced from bioresources, and hence the petroleum-based PET is now being replaced by biobased PET called Bio-PET. The petroleum route usually prepares the first component of PET, i.e., terephthalic acid, and its bio routes are still under development phase [112,113]. Bio-PET is a partially biobased product produced by using bio-derived mono ethylene glycol (Bio-MEG) [31]. Bio-MEG is produced from agro-based resources and includes bagasse, hay, and sugar cane molasses [114]. Bio-PET-based products have similar quality as that of regular PET in terms of weight, appearance, etc., and they can be recycled and reused. Today, Bio-PET is mainly used in the manufacturing of soda and drinking water bottles, automotive interiors, packaged goods, electronics, and construction goods, which makes them an environmentally friendly alternative to traditional plastic.

Polyethylene furanoate

As discussed in the above section, Bio-PET is not 100 % biobased as the significant component of the synthesis, terephthalic acid, is obtained from petroleum resources. As an alternate, polyethylene furanoate (PEF) is a type of thermoplastic, that is 100% biobased and has the potential to replace the PET completely. PEF is generally synthesized by polymerization of ethylene glycol, i.e., Bio-MEG and a 2,5-furan dicarboxylic acid (FDCA); both are biobased chemicals. FDCA is produced from the oxidation of 5-hydroxymethyl furfural, which is a platform molecule derived from the lignocellulosic biomass. PEF has a high glass transition temperature, lower melting point, and excellent barrier properties to water and oxygen in comparison to PET, which makes the PEF not only 100% biobased but also a superior competitor to PET [40]. PEF can be employed in the packaging industry for milk, soft drink, water, and alcoholic beverages. PEF based products are not biodegradable but can be easily recycled or incinerated to convert back into CO₂.

Polytrimethylterephthalate

Polytrimethylterephthalate (PTT) is a partially biobased plastic made by the condensation polymerization or esterification of terephthalic acid and 1, 3-propanediol [115]. 1,3-propanediol is a biobased molecule (referred to as Bio-PDO) derived from hydrogenation of glycerol or by fermentation reaction. PTT has similar physical properties, i.e., heat

resistance, strength, toughness, and stiffness as that of PET. PTT is used in fiber manufacturing, textiles, and carpet synthesis for the domestic market and automobile industry since they are soft in texture but can bear heavy wear [41,42,116]. Due to similar processing properties to polybutylene terephthalate (PBT), PTT can also be used in injection moulding. PTT-based plastics are resistant to shrinking and deformation and can be used in electric and electronic components, air breath outlets, and car instrument panels due to their high-quality surface texture [31,117].

8. Biobased alkyds resin

Alkyd resins are produced by polycondensation of polyvalent alcohol such as sorbitol, glycerin or glycol with a carboxylic acid such as phthalic acid, succinic acid, maleic acid, adipic acid, or their anhydride. Some of these polyvalent alcohols and acids can be produced from renewable resources; hence the alkyd resins can be biobased or partly biobased [43]. Succinic acid, adipic acid, or maleic acid can be produced from the platform molecules derived from biomass resources such as lignocellulose biomass. Similarly, acids, such as fatty acids derived from vegetable oil, are biobased and can be used for the synthesis of various alkyd resins [44]. Combining both biobased derived carboxylic acid and polyvalent alcohol, 100% biobased alkyd resins can be synthesized (e.g., Voxtar M100 synthesized by PersorpAB, Sweden) [74]. Alkyd resins are used as a raw material in paints, lacquers, and also as filler compounds. Additionally, they find applications in the production of printing inks, adhesives, insulating material, floor covering material, and textile enhancers [118].

Biobased polysuccinate

Polysuccinate can be synthesized either by polycondensation of succinic acid with the diols or by ring-opening polymerization of succinic anhydride with ethylene oxide [46]. Depending on the sources of diols and acid, the polysuccinates can be partly or 100% biobased. Polybutylene succinate (PBS) is a biodegradable plastic that is synthesized by using succinic acid and butanediol (BDO) [119]. Bio-based butanediol, i.e., Bio-BDO and succinic acid, are produced from the sugar derived from starch hydrolysis in a single step fermentation by *E. coli* [120,121]. PBS can also have more than one acid to get the diacid polymers suitable for different applications. Polybutylene succinate adipate (PBSA) is a derived product of PBS wherein addition to succinic acid, adipic acid is polymerized within the compound [122]. PBS has a high melting temperature and a wide processing method that is suitable in extrusion, injection moulding, fiber spinning, film blowing, and thermoforming [31,45].

9. Other biobased polyesters

Other partly or wholly biobased polyesters are polybutylene terephthalate (PBT), polybutylene adipate terephthalate (PBAT), and vegetable oil-based polyesters. PBTs are produced from the polycondensation of terephthalic acid and butanediol (BDO) [123]. Similar to the above plastic material, PBT can be fully biobased, but as discussed earlier, the cost of acid is very high; hence at present, it is partly based on bioresources. Similar to PBT, PBAT has adipic acid as additional acid, which gets polymerized along with other acids to obtain the final product. In 2009, BASF, a German chemical company, synthesized fully biodegradable PBAT from renewable resources [124]. These polyesters have similar properties to that of PET and can be employed in injection moulding to produce automotive exterior/interior parts and compostable plastic bags for gardening and agricultural uses [47]. Vegetable oil-based polyesters are resin-type polyester made by the polycondensation of acid or ester with alcohol in which one of the monomers should be derived from the vegetable oil. The monoglyceride method is the most commonly used for polyesters preparation. In this process, oil is processed to get the mono or diglycerides, which are further converted into polyesters by employing polycondensation with anhydrides such as succinic, phthalic, or maleic anhydride [125]. Depending on the anhydride source, it can be partly or 100% biobased plastic. These alkyds can be used for the manufacturing of adhesives, casting material, insulating materials, and printing inks [48,49]. They can also be used as textile finishing agents. Linoleum is one such product produced from linseed oil and is used as a floor covering material [126].

9.1 Biobased polyamides

Polyamides are an essential class of polymer having a wide range of applications. The production and development of polyamides are continuously growing since the establishment of nylon and perlon in 1930 [50]. Polyamides were particularly suitable for the synthesis of fibers and few technical applications. It is still being used in the production of extruded products, hollowware, textiles for the manufacture of decorative material, clothing, and technical fabrics [50]. Polyamides are produced via polycondensation of amino acids or ring-opening polymerization of lactams (cyclic amides), resulting in AABB-types and AB-type polyamides, respectively. In these polymers, the monomers are connected by amide bonds. Bio-polyamides can be wholly or partly biobased depending on the source of dicarboxylic acid (C10) and diamine. The majority of these bio-amides are based on sebacic acid, synthesized from ricinoleic acid derived from castor oil [127]. Apart from this, undecenoic acid can also be prepared from the same ricinoleic acid via pyrolysis and used for the synthesis of bio polyamides named

PA11 that is available in the market since 1940 [128]. It is produced via polycondensation of amino acid, i.e., 11-amino undecanoic acid. Using sebacic acid as a monomer, various partially biobased polyamides such as PA4.10, PA6.10 are produced with "10" components as their biobased part. PA6.10 is prepared by the step-growth polymerization of diacid, which is biobased with hexamethylenediamine as diamine source, making it partly biobased polyamides. Similarly, PA10.10 is produced from the polymerization of sebacic acid and decamethylenediamine (C10) [51]. In this, both components are biobased derived from castor oil. These polyamides have excellent mechanical properties such as high flexibility, tensile strength, toughness, resilience, and abrasion resistance while having lower moisture absorption ability with improved chemical resistance when compared to traditional PA6.6 polyamides [52,129,130]. Due to their superior properties, bio polyamides are used in various applications such as pneumatic air brake tubes, flexible oil and gas pipes, electrical cable jackets, and automotive fuel lines [52].

9.2 Biobased polyurethane

Polyurethanes (PUs) are a versatile class of plastic having a wide range of applications in the coating, foam, adhesive, and fiber industry [131]. PUs are prepared by carrying out a reaction between polyols and diisocyanates, forming urethane linkage, which is a carbamate ester linkage generated during the reaction between the isocyanate and alcohol group [54]. They may be used as a thermosetting or thermoplastic form. Bio-polyurethane (Bio-PUs) can be partly or wholly biobased while utilizing biobased polyols and petroleum-based or biobased isocyanates. Most of the Bio-PUs are partly biobased and derived using biobased polyols obtained from plant oils such as soy or castor oil [53]. Castor oil already contains OH groups, while polyols derived from vegetable oils (sunflower, rapeseed, or soya) are produced by epoxidation of unsaturated fatty acid followed by the addition of multiple alcohols in the epoxide opening reaction. Another route of synthesis of bio polyols is based on starch liquefaction, liquified lignin, and nutshell liquid [132]. Recently, biobased diisocyanates such as pentamethylenediisocyanates have been commercialized that can produce a pure form of Bio-PU. Bio-PUs are biodegradable foams having high thermal and dimensional stability than petroleum-based PUs. Bio-PUs have been used to replace conventional PUs in various applications, particularly for the production of cushions, coatings, and insulations.

9.3 Biobased polyacrylates

Polymerization of various acrylic esters results in the formation of a resin-type structure known as polyacrylates. The commonly used polyacrylates are polyethyl acrylates and polymethyl acrylates. These acrylic esters are made by esterification of acrylic acid,

which is generally produced from petroleum resources [55]. The biobased polyacrylates can be synthesized by using bio-based materials, e.g., glycerol, fatty acids, or sugar. The dehydration of glycerol gives acrolein, which is further oxidized to biobased acrylic acid, which then gets transformed into ester by the reaction with alcohol, ultimately polymerizing to form the polyacrylate. Depending on the source of alcohol and acrylic acid, the polyacrylates can be complete or partly biobased plastic. Currently, several efforts are being made to use a biobased version of platform molecule, e.g., 3-hydroxy propionic acid, lactic acid, etc. [133], for the synthesis of raw materials of plastic. The bio polyacrylates have similar properties to that of the conventional ones. Polyacrylates find application as superabsorbent in consumer products as a thickener and are mainly used in the salt form (sodium polyacrylate) in pigment dispersants [56].

9.4 Biobased polyolefins

Polyolefins (polyethylene and polypropylene) are the most common and essential plastics used in various applications. They have very low density ($>1\text{g/cm}^3$) and hence can easily float in water. Both types of this category can be produced from renewable resources [57].

Biobased polyethylene (Bio-PE)

Polyethylene (PE) is the most used global plastic today, produced by the polymerization of ethylene gas. Ethylene can be obtained from petroleum resources or ethanol dehydration [134]. The latter method was used in the early 20th century before the availability of direct ethylene gas for industrial production from petroleum resources. Biobased polyethylene (Bio-PE) can be obtained from renewable resources such as sugarcane and has a similar characteristic to that of PE obtained from fossil oil. The production of Bio-PE is based on the ethylene produced from ethanol (bioethanol obtained from sugarcane) [31,57]. The process includes the fermentation of sugarcane juice to ethanol, which is dehydrated to get the ethylene, and after polymerization, the formed product is Bio-PE (Fig. 5). Bio-PE is mostly used in the packaging industry [135]. It is an important intermediate for the synthesis of other polymers like PET and polyols for polyurethanes [136]. It can also be used in the production of bags, pouches, petrol canisters, barrels, automobile fuel tanks through blow moulding and injection moulding [58].

Fig. 5 Bio-polyethylene production from renewable sugar cane biomass

Bio-polypropylene

Like Bio-PE, Bio-polypropylene (Bio-PP) can also be synthesized from bioethanol using more sophisticated methods [137]. The part of ethylene obtained, as mentioned above, will dimerize to butenes, which will react with remaining ethylene to produce Bio-PP. One more way to it is via vegetable oil cracking in the fluid catalytic cracker (FCC) [138,139]. Bio-PP is generally used in injections, packaging, textiles, and due to its light-weight feature, it can also be used in automobile industries for the production of seat-backs, shelving, interior storage bins, and load floors [17,140].

9.5 Biobased polyvinyl chloride

Polyvinyl chloride (PVC) is the polymerized product of the vinyl chloride (VC) monomer. VC is synthesized from ethylene gas via oxychlorination methods. As discussed in the section of bio propylene synthesis, the fermentation of sugarcane yields ethanol, which can be converted to bio ethylene gas. The bio ethylene gas can be used as a starting material for the synthesis of biobased VC (Bio-VC) that can be further polymerized to obtain Bio-PVC [31,141]. They have similar properties to that of general PVC obtained from petroleum resources. Bio-PVC is used in the manufacturing of wires, films, cables, pipes, and bottles with end-use in various industries, including transportation, packaging, electrical and electronic instrument, and construction [17,58].

9.6 Epoxy resins

Epoxy resins are thermosetting polymers having several desirable properties such as low shrinking with strong adhesion and hardness property while offering excellent stability for many solvents and alkali solutions [59,142]. Most of the epoxy pre-polymers are synthesized by condensation of bisphenol A and epichlorohydrin that produces diglyceride ether of bisphenol A, a most commercially available form of epoxy resin. Bio-based epoxy resins can be prepared using renewable resources such as vegetable oil, lignin, rosin, furan, sugars, and itaconic acid. Biobased molecules (e.g., FDCA from furan, eugenol from lignin, etc.) react with the epichlorohydrin (another biobased compound) to obtain the 100 % biobased epoxy resins [59]. These biobased epoxy resins

have similar properties to petroleum-based epoxy resins and find applications in the synthesis of structural polymers, epoxy foams, adhesives, coatings. Moreover, it has also been explored in several applications in the aerospace and electronics industry.

9.7 From waste (by processing industrial bio-waste)

Bio-based industrial waste is another huge opportunity to develop bioplastic materials. Researchers are trying to find means to use waste materials for the production of bioplastics. A potato industry (for chips) in the Netherlands, trying to use wastewater produced during the process of peeling and slicing the potatoes. This large amount of processed water contains a high percentage of starch that can be further processed and used. These industries have successfully developed methods to obtain bioplastic from the waste produced. Similar approaches to use processed wastewater containing starch and associated waste are also being applied in several other parts of the world [31].

Tannery trimming waste

Trimming hydrolysate comprising bio-crosslinkers (non-toxic) can be obtained from tannery solid waste for the production of bioplastic material. Trimming hydrolysate powder can be blended with polyvinyl alcohol to obtain transparent and highly flexible films where a solution casting process can be employed. Using citric acid as a plasticizer, the resultant bioplastic films can lead to a smooth, uniform, and defect-free form of plastic with a better tensile strength (>20 Mpa). Moreover, it also showed a notably high elongation capacity (break value >343 %). Following the soil burial test, the bioplastic degraded up to 62 % within 70 days. Also, transparency and the anti-microbial properties of the films were found to be superior due to the presence of citric acid interactions. Therefore, bioplastics derived from trimming hydrolysate could potentially replace fossil-based plastics while having several applications in the field of medicine (wound healing), packaging, among many others [143].

Feather quill waste

The poultry industry generated about 3-4 billion pounds of feathers each year as a by-product in the United States only [144] and more than 157 million pounds in Canada. Feathers comprise around 90 % of protein called keratin, are sent to landfills, which increases environmental impacts and health hazards [145,146]. Several attempts were carried out to use this waste to produce bioplastic. A twin-screw extruder was used for suspending poultry feather quills while using sodium sulfite as a reducing agent. Ethylene glycol as plasticizers was able to mix more effectively with quill keratin at the molecular level, manifesting only one sharp glass transition with excellent mechanical and transparent properties related to other plasticized resins. The melting temperature (T_m)

and the glass transition temperature of quill material were reduced by the addition of plasticizers. The mechanical properties of the materials were also seen to be reliant on the kind of plasticizer used. It was also noted that propylene glycol and diethyl tartrate were able to transform quill material into comparatively hard and brittle polymer related to ethylene glycol and glycerol. However, the material with superior mechanical properties along with better clearness, flowability, and processability was observed by the ethylene glycol as a plasticized resin compared to others [147].

Fruit waste

Industrial fruit juice production generates a large amount of fruit waste, which holds about 60% of fibers in dried biomass. Bioplastics prepared using the fruit waste can also serve as a possible option for conventional plastic materials. Bioplastic can be produced by using fruit waste such as potato and banana peel, among many others. Banana peel blended with glycerol could help generate a polymer that can be used in bioplastic production. The plastic produced could have characteristics of better flexibility and strength. However, potato peels can outperform banana peels since they contain more amounts of starch and polymer chains that are required for the synthesis of good quality plastic [148].

Edible vegetable waste

The agro-food industry produces huge amounts of inedible debris, originated from processed edible vegetables and cereals. More than 24 million tons of processed vegetable waste is produced per annum in Europe alone [149]. Edible cereals and vegetable waste from industries that are rich in cellulose can be converted into bioplastics by just aging them in trifluoroacetic acid (TFA) solutions regardless of their bio-origin. Biopolymers produced from these wastes were found to exhibit distinct mechanical properties varying from brittle and hard to soft and stretchable, depending on the bio-source used in the process. All-natural plasticization of amorphous cellulose is obtained by combining these vegetable waste solutions with TFA solutions of pure cellulose. Bioplastics produced from edible vegetable waste can replace many non-degrading plastics, conserving the environment while being employed in the packaging and biomedicine industry [150].

Waste frying oil (WFO)

Rapeseed oils for the purpose of frying are commonly used in Europe. In other countries of the world, the type of frying oil can differ. The Polyhydroxyalkonates (PHAs) with valerate monomer have been produced successfully from rapeseed oil waste [151]. In PHA production, it can be used without filtration and could produce more biopolymer when compared to pure vegetable oil as a source of production. Waste frying oils from

the food industry can also be employed for the production of PHB. While waste frying oil is plentiful, the main obstacle is to put the collection arrangements in place to collect this waste resource. However, if processed properly, waste frying oil could establish as a cost-effective and environment-friendly alternative to traditional plastic [152].

Papermill wastewater

Production of Polyhydroxyalkonates (PHA) was investigated by treating wastewater of paper mills with a microbial community (*Plasticicumulansacidivorans*). The overall process can be carried out as follows: (1) acidogenic fermentation of paper mill wastewater was carried out in a simple batch process, (2) a feast-famine regime was employed in a sequencing batch mode to provide enrichment of PHA-producing microbial culture, and (3) finally, cellular PHA content was enriched and accumulated in a fed-batch system. This study unveils the potential of wastewater produced in the paper industry to render PHA-based materials. Similarly, these PHA-producing microbial communities can be further explored for the treatment of other types of wastewater while obtaining bioplastic in the process [153].

Conclusion and future prospects

Owing to the obstacles induced by petroleum-based plastic, along with their high cost due to the fast-paced depletion of fossil fuel, they have attracted the use of renewable biomass for the synthesis of bio-based and bio-degradable plastic. Several renewable resources have been identified and employed in the last few decades, and a few are still under development to make them efficiently utilized while attaining a better quality of the bioplastic material. The bioplastic can be biodegradable or non-biodegradable, depending on the monomer type present in the structure. The renewable feedstocks are further classified based on their use in the food chain. So far, the most utilized feedstocks are the carbohydrates and starch originating from plants, i.e., first-generation feedstocks; however, the food crisis in 2008 has stirred the research towards the synthesis of bioplastic from the biomass (derived from the non-food chain), mainly lignocellulose and industrial waste. Bioplastics can be derived from biomass by employing different methods, depending on the type of biomass used in the process. The bioplastics have almost similar properties to that of petroleum-based plastic and can be applied to a related application similar to traditional plastics. Lignocellulose has gained lots of attention in recent years as it contains lignin and cellulose as the main constituent, which is a natural polymer and can also be utilized to generate bio monomer (raw material for polymers) via different treatment methods. Since the large-scale utilization of lignocellulose and waste from plant or biobased industrial waste are still not economically established, more research is required before moving entirely away from a first-generation feedstock for

bioplastic synthesis. Some of the major concerns about existing renewable resources are to have low efficiency as their production drops due to several factors such as weather conditions, land quality, and available area. Algae could be a potential alternative that has the advantage of no land requirement and can be produced in a large amount with the use of a simple photosynthesis process. They can be produced using wastewater from different sources where CO₂ gets utilized for their growth, which makes algae biomass a very attractive option. Moreover, it serves the dual purpose where it can be used as a feedstock while controlling the CO₂ in the environment. However, the high cost of production of bioplastic from algae and several other biomasses has been a concern among the research community, and the broader adoption of bioplastic at the industrial-scale is yet to be seen. Nevertheless, bioplastic could be a savior of the planet earth since the biosphere is on the verge of a global environmental crisis.

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