Biodegradable Polymers, Blends and Biocomposites

Trends and Applications

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Chapter 6

Agro-based Bioplastic Production and Its Application

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6 Agro-based Bioplastic Production and Its Application

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6.1 INTRODUCTION

Plastic is an invulnerable material that can be recast into different forms and utilized in a wide range of applications due to its lightweight, hygienic, and corrosion-free. Day-to-day lifeand the survivability of human beings without plastic is an unimaginable part of the modern world (Umesh et al., 2018). The attractive qualities of plastic are high heat combustion, cost-effectiveness, ease of production, transparency, softness, flexibility, and increased availability in the local community. Plastics play a vital role as innovative materials for use in engineered tissues, absorbable sutures, prosthetics, and other medical applications (Andrady and Neal, 2009).

The necessity and usage of plastics are not only dependent on their mechanical and thermal properties;they aremainly familiar with stability and durability (Rivard et al., 1995). Initially, the first man-made plastic is Parkesine, which was derived from the cellulose biological compound and it can be moulded to any shape (Shah et al., 2021). Later, the natural materials were replaced by chemical polymers (synthetic polymers) which end up in waste all around the environment. Synthetic polymers like polyamides, nylon, polystyrene,teflon, polyethylene terephthalate and polyethylene are derived from petroleumbyproducts. The consumption and user-friendly nature of synthetic plastic results in the depletion of fossil fuels, difficulty in solid waste management and harm to nature (Sharma et al., 2017).

Plastic usage is directly proportional to the accumulation of waste on land and in the oceans (de Moura, et al., 2017). Most types of plastic are not biodegradable but photodegradable, and they slowly break down into small fragments known as microplastics. Due to high UV irradiation and abrasion by waves, the degradation of the microplastic process is much slower in the ocean due to cooler temperatures and reduced UV exposure. Accordingly, plastic is made up of various toxic chemicals which cause serious environmental threats to modern society and result in soil, air, water and also obstruct the groundwater movement (Silva et al., 2014).

The main disadvantage of plastic waste may usually be in the form of film and contain harmful heavy metals, which, when mixed up with water or rainwater, result in crumbling soil fertility. Hydrocarbon-based plastic waste will have a comparatively high calorific value when used for incineration or boiler, but at lower temperatures, the burning of plastics may release deadly poisonous chemical gases into the

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air, including dioxins, which are corrupting to human beings. Using the reprocessing line, Plastic waste can also be used to produce new plastic-based products (Saiki and De Brito, 2012). A serious environmental concern is created mainly by the usage of plastic bags, since they last in surroundings for up to 1000 years and do not decompose. Accumulation or disposal of a large quantity of plastic bags ends up in pollution of land, water bodies, and air, destroying the biosphere and directly or indirectly affecting living organisms (Raghatate Atul, 2012).

Plastic particles and their chemical additives cause environmental and health hazards to living organisms in the world. Generally, plastic debris entershumans directly or indirectly through parasites as vectors and causes particle toxicity and chemical toxicity (Vethaak and Leslie, 2016). Using the animal model studies, the researchers proved that microplastic traverse into the cell membranes, the blood-brain barrier, and even the human placenta results in oxidative stress, lung and gut injury, cell damage, and inflammation (Kershaw and Rochman, 2015; Gasperi et al., 2015; McCormick et al., 2014; Galloway, 2015).

Geyer et al., (2017) published the first global data on the production, usage and end-of-life of plastics. He clearly declared that current extensive and expanding use of plastic as same is continue, roughly 12,000 Mt of plastic waste will be accumulated in the natural environment by 2050. Considering the environmental and health issues caused by plastic and its Greenhouse gas emissions pays the way to find alternative ways towards a circular economy, which helps to decrease the non-renewable resources production throughreuse and recycling of the materials (Rosenboom et al., 2022). The increasing concern aboutsynthetic plastics issues has made scientistsattracted towards "green" plastics such as bioplastics which are produced from renewable resources (Siracusa and Blanco, 2020). To avoid the nondegradable petroleum product, sustainable, significant and inexpensive methods is needed to produce the best-quality of biobased renewable materials (Bohmert-Tatarev et al., 2011).

Bioplastics are vouched as a noteworthy alternative to plastics because their production is not dependent on fossil fuels and is cost-effective. In 2020, European Bioplastics declared that according to the development of the bioplastics market, nearly 1% of bioplastics, more than 368 million tons of plastic produced every year. Due to increases in the demand for the use of plastics, the bioplastics market is growing and diversifying all over the world. In the same year, the report declared that the capacity of bioplastics globally is expected to increase roughly from 2.11 to 2.87 million tons in 2025. It is the best substitute for every conventional plastic material.The commercialization bioplastics such as polyethylenefuranoate (PEF), polypropylene-based (PP), polyhydroxyalkanoates (PHAs), and polylactic acid (PLA) are expected to grow in their manufacturing process over the next few years (Shen et al., 2009).

Biopolymers are synthesised from biomass feedstock or a combination of sustainable, eco-friendly substances, and it has been reported that the manufacturing capacity of bioplastics has increased from 0.36 Mt in 2007 to 3.45 Mt in 2020 (Agustin et al., 2014). It has the capability to diminish the landfills, enhance the degradation and eliminate the toxins which create air pollution. The significant essential for the production of bioplastics is mainly dependent on the usage of economical raw materials and methodology adapted for the production. Bioplastic products are mainly produced from various sustainable feedstocks, which are available in plenty and are called agro-waste products (Nee and Othman, 2022). Agro-based polymers are one of the best and most well-known polymers.

Agricultural waste is normally incinerated or dumped, which causesenvironmental problems. It contains polysaccharidesand carbohydrates, so it gives alternative ideas to use as a starting material to produce biobased polymers. The incorporation of agricultural residues into the polymer is highly innovative because it has high strength, stiffness, availability, recyclability, low cost, environmental friendliness, no toxicity, lower pollution emissions and low density of natural fibres (Pirayesh et al., 2013; Borri, et al., 2013; Reixach et al., 2013; Hamza et al., 2013; Battegazzore et al., 2014).Therefore, ignored wastes like agricultural residues should be put in the attention and purposely studied as substrates for sustainable energy.

6.2 CLASSIFICATION OF PRODUCTION OF BIOBASED MATRIX

Biobasedmatricesare ecologically benign,biocompatible, and biodegradable. The origin of biopolymerisgrouped into four classifications, as shown in Figure 6.1. The classification is based on the synthesis of polymers from chemicals and bacteria, as well as blends with polymers and from biomass or natural resources (Satyanarayana et al., 2009).

6.3 NEED OF RECYCLING OF AGRICULTURAL WASTE

Agricultural wastes areunwanted materials produced entirely from agricultural operations directly related to the growing of crops or the primary purpose of making a profit by rising of animals or by agro-industries. Plant waste from agriculture poses a high negative impact problem on the environment due to their landfills, soil pollution, and incineration process. Agricultural waste is often disposed of in open trash

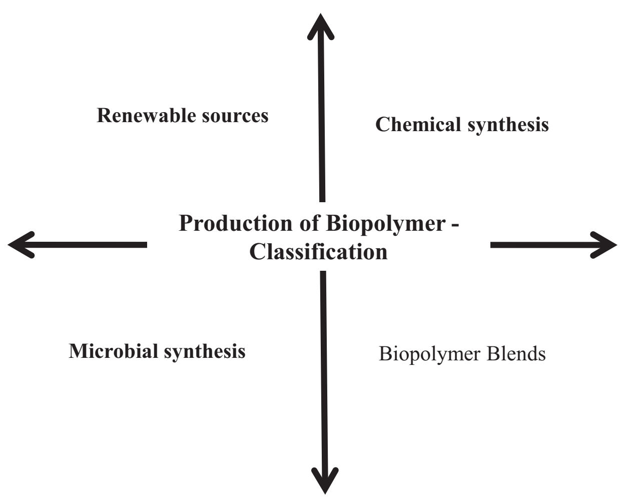

FIGURE 6.1 Classification of production of biopolymer.

dumps, where it can contribute to severe soil contamination and increase the dangers already present because stored garbage can emit toxic gases. The great strategy to control environmental pollution is only by the management of agricultural waste (Mostafa et al., 2018).

Because the cost of recovery and collecting for reuse is more than the lucrative value of various forms of waste as the end products from the agro-industries, are discarded, which has a negative impact on the environment (Panesar and Kaur, 2015). Nearly, 90 million tons of oil equivalents of agricultural waste were resulting from enormous supply chains (Gontard, et al., 2018). Only a small portion of the massive waste accumulation is used in the manufacturing of animal feeds, manure, and other value-added products, and the remaining tons of waste are causing pollution and environmental hazards. However, the successful utilization of waste could be a good remedy for the development of degradable products, if appropriate biotechnological interventions are available (Panesa and Kaur, 2015).

The agro-wasteisrich in micro and macronutrients especially starch and cellulose, which can be extracted and moulded into new forms. Using this principle, the reinforcement of agricultural residues into biopolymer is presently an interestingtopic in the research field due to their compatibility, recyclability, lowcost, and energy consumption (Borri et al., 2013; Reixach et al., 2013; Hamza et al., 2013; Battegazzore et al., 2014). Moreover, it is rich in fermentable sugars, which microbes can directly utilize and convert into high-value components (Ali and Zulkali, 2011). One example of byproducts is organic acids such as lactic acid, which are obtained from industrial and agricultural waste as substrates.

6.4 AGRO-WASTE INTO BIOPLASTICS

The general process of producing bioplastics from agro-waste materials is pretreatment, extraction and characterizing of materials (Hagemann and D'Amico, 2009), as shown in Figure 6.2.

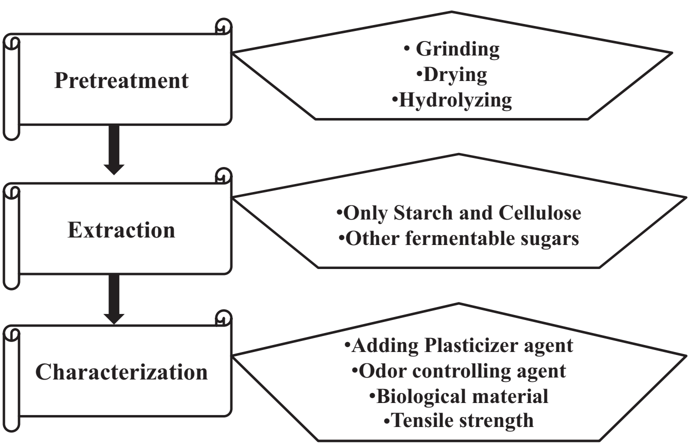

FIGURE 6.2 Steps involved in conversion of agro-waste into bioplastic.

6.5 CRITERIA FOR THE SELECTION OF AGRO-WASTE RESIDUES

The use of agro-wastes in the production of biobased matrix is primarily due to the large quantity of starting materials/precursors available, cost-effectiveness, andavailability. India and China are the two most powerful economies with the potential to increase the production of fruit and vegetable-based biopolymers (Sharma et al., 2020). Figure 6.3 shows the important criteria for selectingagro-waste for bioplastic production.

The lignocellulose fibres are rich in waste materials like pineapple, sisal, jute and curaua (Satyanarayana et al., 2009), and the end products are determined by extraction method. The mechanical strength of produced biomaterials is increased by the large quantities of cellulose, so selecting the precursors with cellulose is important (Maraveas, 2020). For example, corn and stalks are rich in cellulose, which is the major waste generated from agriculture.

6.6 STAGES OF BIODEGRADATION

Biodegradation is defined as the degradation of materials in the presence of biological activity. Biodegradation occurs in three stages: (i) biodeterioration – the physical, chemical, and mechanical properties of the polymer are altered by microorganisms; (ii) biofragmentation – polymers degrade into oligomers and monomers as a result of microbial activity, and (iii) assimilation – it is a continues fragmentation process. Fragmented carbon polymers are converted into carbon dioxide, water, and biomass (Lucas et al., 2008).

Degradability of synthetic polymers is impossible because of their chemical structure, complexity, chain of polymers, and crystallinity structure. Polymers with shorter chains, less complexity, and amorphous structure are typically easily degradable by microorganisms, and environmental factors such as pH, temperature, and moisture play an important role in biodegradation (Massardier-Nageotte et al., 2006; Kale et al., 2007).

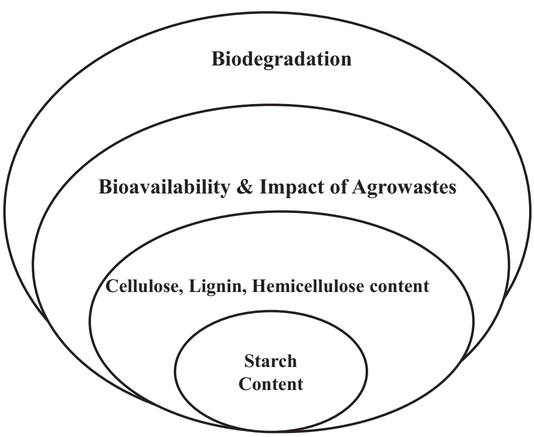

FIGURE 6.3 Criteria for the selection of suitable agro-waste residues.

6.7 PRECURSOR FROM AGRICULTURAL WASTES

6.7.1 Cellulose and Its Sources

Cellulose is the most abundant biomass material on the planet, and it is well-known as natural fibres or regenerated fibres obtained from cotton, jute and rayon (Iwata, 2015). Cellulose is one of the important sources for bioplastic production, but it does not have a plasticity characteristic. The derivatives of cellulose are cellulose nanocrystals (Arrieta et al., 2015), nanofiber cellulose (Siró and Plackett, 2010), and acetate butyrate (Grunert and Winter, 2002) are used directly in the production of bioplastics. Even though, cellulose lacks plasticity nature, itspresence in bioplastics preparation will increase the physical properties of polymers and as fillers. Biocomposites are natural filler-based materials that have been successfully produced and marketed. The familiar choice of filler in thermoplastic materials is cellulose (natural fillers), which isinexpensiveand obtained from renewable resources like coconut shells, palm kernel shells, oil palm empty fruit bunch, and rice husk (Chun et al., 2012; Salmah et al., 2013; Chun et al., 2013).

6.7.2 Cellulose from Cocoa Pod Husk

Cocoa is an important agricultural crop in several tropical countries (Vriesmann et al., 2012), and Cocoa Pod Husk is a waste generated from cocoa pod net weight ranging from 52% to 76% (Koay et al., 2013). Lubis et al. (2018) revealed that bioplastics were produced from starch of jack fruit seed reinforced with cellulose of cocoa pod husk. In this method, glycerol acts as a plasticizer. Using alkali treatment, bleaching and hydrochloric acid hydrolysis, microcrystalline cellulose was produced. It showed 74% crystallinity was confirmed in XRD, and rod shape (5–10 μm length) with adiameter of 11.635 nm was proved by SEM.

Azmin and Nor (2020) proved that cellulose and fibre were extracted from cocoa pod husk and sugarcane bagasse and incorporated together to form bioplastic materials. Their observations showed that the ratio of cellulose to fibre is 75:25,carriesgood water absorption and plays the best role in food packaging. The produced materials proved to bethebest antimicrobial by reducing the growth of mould and preservingthe food for a longer time by preventing the moisture transfer between the environment and food. Due to the presence of hydrophilic nature of bioplastic derived from cellulose, decreases the water vapour barrier, which leads to brittleness and reduced mechanical properties.

6.7.3 Cellulose from Oil Palm Empty Fruit Bunch

Accumulation of palm fruit waste after crude oil extraction is 28.65 million Mt each year in the land. It is eradicated by burning or dumping in the land, resulting in air pollution. Palm fruit waste contains more cellulose (40.37%) than hemicelluloses (20.06%) and lignin (23.89%) (Isroi et al.,, 2017). Due to the high content of cellulose in palm fruit waste, it is used as a good source of cellulose derivatives.The cellulose from the waste is isolated and bleached to remove lignin using sodium hydroxide and sodium hypochlorite methods, and the cellulose content is increased by about 97%.

Oxidation of cellulose helps to decrease the crystallinity and improve the carboxyl side chain of the components. Finally, for bioplastics production the purified cellulose is mixed with glycerol (plasticizer) and cassava starch as composites. It clearly ends up in the production of bioplasticsheets using casting methodology (Cifriadi et al., 2017).

6.7.4 Cellulose from Pineapple Peel

Carboxymethyl cellulose (CMC)hasahigh degree of solubility and is used as a resource for fabricating bioplastics, extracted from agricultural wastes. Pineapple is apopular edible fruit and is produced as a solid waste during processing. The accumulated wastes are rich in cellulose andcan be extracted by refluxing with acidic or alkali solution (Xu et al., 2009). Using etherification, CMC is produced from pineapple peel cellulose. Chumee and Khemmakama (2014) proved the CMC extraction by etherification and refluxing of pineapple peel powder.

6.7.5 Cutin and Its Sources

The outermost membrane of plant cuticles is composed of cutin, which protects the plant epidermis of aerial organs. The size and thickness of plant cuticles range between 0.02 and 200 m (Nawrath, 2006). Pure cutin and its monomers are rich in biopolyester, non-toxic, biodegradable, waterproof, UV-blocking and amorphous. It also plays an important role in the protection against pathogensand abiotic factors and also in avoiding water loss from internal tissues. These features increase the interest in considering cutin as a realistic, raw material in food-packaging material instead of conventional plastic (Zhang and Uyama, 2016; Heredia-Guerrero etal., 2017).

The main source of cutin biomass is tomato pomace. Due to the low price and more harvesting, tomatoes are used for multiple purposes, particularly atthe industry level. In the tomato processing industry, the skin of tomato (tomato pomace) accumulation is more because of its high production of juice, paste, pureeand sauce. About 20wt% of polyester is present in tomato pomace, which is considered agood raw material for bioplastics production. Using the melt polycondensation method, from the tomato pomace unsaturated and polyhydroxylated fatty acids were converted to free-standing films in the presence of catalyst Tin(II) 2-ethylhexanoate (Heredia-Guerrero etal., 2019). Benítez et al. (2018) produced unsaturated fatty acids without a catalyst. Finally, inexpensive resource for the fabrication of bioplastics has been synthesized from tomato pomace agro-waste, which has the features of amorphous, hydrophobic nature, insoluble, infusible, and thermally stable.

6.7.6 Starch and Its Sources

Starch is a naturally occurring polymer that is one of the major carbohydrates. It is derived from agricultural resources such as corn, wheat, rice, tapioca, amaranth, cashewnuts, and potatoes in the form of granules (Ren et al., 2009).After extraction, it is white in colour, tasteless, odourless, and undissolved in cold water or alcohol, easily available with low-cost, non-toxic and biologically absorbable (Sanyang et al., 2018). It is also renewable, biodegradable, considered as avalid choice of sustainable resources and capability to reveal thermoplastic properties.

In plant tissue, each granule of starch contains polysaccharides such as amylopectin (70%–80%) found in million molecules which are accompanied by amylose (20%–30%).The structure of both polysaccharides has D-glucose units in$^4C_1$ conformation. The length of the amylose chains ranges from 10^2 to 10^4 glucose units, and amylopectin varies from 10^4 to 10^5 glucose units (Ponstein, 1990). Starch is semicrystalline in nature due to its 20%–40% crystallinity (Mentzer et al., 1984), and the presence of hydrophilic propertiesmakes itincompatiblewith all hydrophobic polymers. Due to these properties, starch plays an important role as an alternative to replace thermoplastic.

Native starch cannot be used directly as traditional plastic because ithas limited high water affinity, brittleness, limited long-term stability caused by water absorption, ageing caused retro gradation, poor mechanical properties and bad processability. Thermoplastic starch is produced by using disruption, plasticization and the application of mechanical and thermal treatment (Mathew and Dufresne, 2002; VanderBurgt et al., 1996). Blending plasticized starch with some other degradable polymer is also thebest solution to produce cost-effective materials (Gaspar et al., 2005).

Usage of starch as thermoplastic in polymer technology is based on two forms:starch-filled plastics and structural starch modifications. In starch-filled plastics, the microbial uptake of the starch leads to increased porosity by increasing the surface area. In structural starch modifications, using heat and mechanical methods, the native starch forms are modified, and methods are listed (Bastioli et al., 2013). The significance of starch-based biodegradable plastics is that they decrease the cost and usage of synthetic plastics, which enhance the biodegradability of the products (Wool et al., 2000).

Plasticizers play an important role in the blending of starch into plastic, and they are a low molecular weight substancethat reduces the hydrogen bonding of the chains, which helps to increase the flexibilityand processability of polymers. Hydrogen bond-forming abilities aresignificant between plasticizers and starch molecules, which arethe main properties of starch-based bioplastics. The physical characteristics of the processed starch depend on the plasticizers quantity and its types by controlling destructurization and depolymerization of the final materials (Averous, 2004).Various plasticizers such as water, amide, sugars, glycol, quaternary amine, urea, glycerol and sorbitol are used to prepare thermoplastic starch blends (Shi et al., 2007).

In 2020, it was reported that starch-based plastics havethe largest production capacity of about 1.3 Mt, and the remaining depends on the production of polylactic acid (PLA) and polyhydroxyalkanoates (PHAs) (Shen et al., 2009).

6.7.6.1 Starch from Potato Waste

Potato is the world's fourth major crop next to rice, wheat and maize (Leo et al., 2008). Inthe world, India stands in third place as the largest potato producer after China and the Russian Federation, with nearly 41,483 thousand tons of potato produced

(FAOSTAT, 2016). Every year, nearly millions of tons of skin waste are generated in the potato chip industry and for disposal,a significant amount of money is required for transportation (Rogols et al., 2003). Composting or using it as feed for animals is a conventional management strategy for discarding peel waste to avoid pollutants (Nelson, 2010). The waste contains large quantities of starch, cellulose, hemicelluloses, carbohydrates and proteins, which lead to thedevelopment of biodegradable polymers.Due to the presence of excess starch in potato peels, it is a potential application for the development of biopolymer film (Kang and Min, 2010).

Xie et al. (2020) proved that the combination of potato peel with bacterial cellulose (BC) and curcumin leads to the formation of active potato peel films, and these bond interactions strengthened the mechanical properties of the films, water vapour permeability and the light transparency. During the time of packaging, curcumin present in the films inhibits the lipid oxidation of fresh pork at the time of storage. He clearly reported that potato films with BC will have potential in packaging companiesand are the best solution for replacing thermoplastic polymers.

Degradability of potato peel bioplastics was determined by Arikan and Bilgen (2019). They concluded that using potato peels, waste bioplastics can be produced, and it will be completely degraded within 28 days compared with commercial bioplastics. Using ultrasound treatment, biopolymer film development was done by incorporating potato peel waste and sweet lime pomace. It clearly reported that an increase in the ultrasound treatment gives the best properties of biopolymer film such as weight loss, hardness and microbial load reduction(Borah et al., 2017).

6.7.6.2 Starch from Jackfruit Seed

In Asia, the most tropical popular fruit is jack fruit, which contains about 100–500 seeds in single fruit and is enriched with protein and starch. Mukprasirt and Sajjaanantakul (2004) compared the cotyledon starch with modified starch, and it clearly revealed that seed starch isrich in amyloseand protein contents, requiresless temperature for gelatinizationand has high stability compared with modified starches. They concluded seed starch can replace the modified starch.

Starch is an important precursor in the production of biodegradable films due to its renewable and inexpensive sources. About 8%–15% of jackfruit seed is made up of starch, and it is used in bioplastic production. From the seeds, starch was extracted using grinding and deposition methods. After deposition, the starch-rich suspension was filtered using Whatman filter paper and dried at 70°C. The dried starch powder was reinforced with cellulose as filler using plasticizer (glycerol), and finally, bioplastics wereoptimized with different ratios. This research reflects the usage of jackfruit seeds as starch source to produce bioplastics (Lubis et al., 2018).

6.8 ROLE OF MICROBES IN AGRO-BASED PLASTIC PRODUCTION

6.8.1 Polyhydroxyalkanoates (PHA)

PHAs are important biopolymers that are produced by the bacteria and stored inside the cell in the form of inclusion bodies as reservoirs (Shrivastavet al., 2010).Several studies declared that various PHAs are produced by different bacterial strains, and due to their biodegradable properties,they arean alternative to petroleum-based plastics (López-Cuellar et al., 2011). The composition of monomers of PHAs is directly related to the available carbon source and to the bacteria species. The selection of raw materials to produce PHAs is difficult, since it depends on the cost-effectiveness. It can be solved only by the use of industrial byproducts like farming, domestic waste materials, fats and cellulose-rich wastes (Rasu and Arun, 2017). The best PHAs can be produced by agro-industrial waste as substrates since it is rich in all needed compounds.

In everyday industrial life, the food industry generates waste palm oil, which is the best feedstock for the production of polyhydroxylalkonates (PHA). In the world of biopolymer production, using waste palm oil will decrease the costs and the adoption of PHA. The waste palm oil contains fatty acid-long chains as a carbon source, and during the fermentation by bacteria,it is converted into structurally different PHA with 6–14 carbon atoms. Using saponified waste palm oil as a carbon source, *Pseudomonas* sp. G101 was able to produce an increased amount of biopolymer (PHA) with the best thermal and physical properties (Możejko and Ciesielski, 2013).

Vega-Castro et al.(2016) produced and characterized the PHA from solid waste of pineapple and fermented by the bacteria *Ralsthonia eutropha*. By optimizing different fermentation conditions, PHAs wereproduced and using FTIR, GCMS, and NMR, the produced compounds were characterized. They proved at pH 9, 60 hr fermentation, the best PHAs were obtained, and it is auseful alternative for processing of waste generated in agro-industries.

6.8.2 Lactic Acid

Lactic acid is the basic chemicalused to produce PLA, and the most commonly biodegradable plasticused today. LA can preventthe growth of many pathogenic microorganisms, and it is used as flavour, acidulant, and preservative in food. It also acts as a scraping solution in high quantities and an important ingredient in skin care creams designed to remove dead cells from the surface of the skin (Komesu et al., 2017; Smith, 1996). LA is essential in the production of poly (lactic acid) (PLA) and poly (lactic-co-glycolic acid) (PLGA), the most common eco-friendly bioplastics at present (Anderson and Shive, 1997; Tyler et al., 2016).

Using biotechnological techniques, lactic acid is produced from agricultural residues and isanimportant componentin producing biocompatible polymers. The produced polymers are used in high-end applications, but their production and recovery costs are extremely expensive.The exact method to produce LA is fermentation by bacteria, fungi and yeast (Gao et al., 2011). *Carnobacterium*, *Enterococcus*, *Lactobacillus*, *Lactococcus*, *Leuconostoc*, *Pediococcus*, *Streptococcus*, *Tetragenococcus*, *and Vagococcus* are the lactic acid-producing bacteria. The LA producer's (LA bacterias) characteristics are not similar toeach other since their morphological, physiological and biochemical features are different in nature, and each should be considered for fermentation on exact raw materials. The metabolic engineering techniques and optimization of LA production improvement aregoing on (Upadhyaya et al., 2014).

Cui et al. (2011) showed that using mixed culture system, glucose was converted into LA by *L. rhamnosus* through the Embden–Meyerhof–Parnas (EMP) pathway,

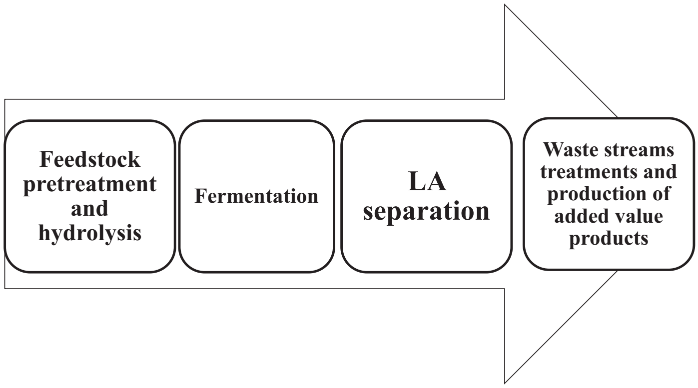

FIGURE 6.4 Stages in lactic acid production.

and at the same time, xylose from the cornstoverwas converted to LA by *L. brevis* strain. The foremost company, Nature Works LLC, USA, stands as a leading manufacturer of PLA and PLGA from agro-residues like corn starch, sugar beet, and sugarcane as raw materials. The lab-scale production of PLA resin is dependent on corbion, and there is extensive research being conducted around the world to derive the LA using second-generation materials such as bagasse, corn stover, and wheat straw as sources to produce the PLA. Reports on the processing of PLA obtained by polymerization of LA from waste and byproducts of agriculture are scarce. Both academia and bioplastic producers are urged to conduct more intensive research in the domain of lactide production methods by using second-generation feedstock for its polymerization in order to demonstrate the feasibility of PLA production from specific agricultural substrates.Generally, four major stages may possiblybe distinguished in fermentative LA production (Figure 6.4).

6.8.2.1 Feedstock Pretreatment and Hydrolysis

The valorization process of LA production directly depends on the substrate chemical composition. The primary precursor of agricultural residues is solid, and in the secondary, either solid or liquid. During processing, the storage time, unwanted bacterial growth, and deterioration are analysed based on the water content present in the substrate. The complex carbohydrates are hydrolysed in the pretreatment, which helps the microbes to access the simple compounds in substrate to produce the LA. Because some substrates are high in readily available monosaccharides, microorganisms can be used without any pretreatment (Ohkouchi and Inoue, 2006; Venus et al., 2018; Lu et al., 2010).

In LA production, particular microbes hydrolysed the carbohydrates into fermentable sugars. The production of fermentable sugars from carbohydrates is called saccharification. The enzymes play an important role in the hydrolysis of starch through gelatinization, liquefaction, and saccharification. The optimization of hydrolysis for different substrates is necessary to find the enzyme selection, temperature, mixing conditions, etc. (Panesar and Kaur, 2015).

6.8.2.2 Fermentation

The LA production mainly depends on the pH, and it varies from 5.0 and 7.0, and it will prevent the inhibition of the cell growth (Wang et al., 2015). Nearly 90% of LA was produced using $Ca(OH)_2$ as neutralizing agent, and calcium lactate was formed. The liberation of LA from calcium lactate was achieved by using H_2SO_4, and finally,a significant amount of gypsum ($CaSO_4$) was yielded (Yang et al., 2013). The produced gypsum results in global warming (Pal et al., 2009; Groot and Borén, 2010), and presently so, many research works are being carriedout to convert it into PLA, which is planned to be usedin medical applications (Murariu and Dubois, 2016). Batch process is easy to operate with low contamination, which is the single-step mode. But the substrate and product inhibition will be more (Abdel-Rahman et al., 2013; Cubas-Cano et al., 2018).In fed-batch mode, inhibition of substrate is low, and microorganisms are maintained in a prolonged lag phase, which helps to increase the production of LA (Shi et al., 2012). Effective fermentation depends on the feeding of sterile media into the fermentor exponentially or constantly or intermittently in exact time intervals.

In LA fermentation, the highest productivity can be reached in the continuous culture method at steady-state condition. In this method, due to the constant rate and fast growth of microbes, LA is produced as primary metabolite. Compared with other fermentation, conventional continuous fermentation results in higher productivity. The production rate is higherdue to outcome product inhibition, more dilution rate or shorter residence time. The only longer-term yield of LA depends on constant fermentation, especially by reducing or omitting the time essential for inoculum preparation, which allows microorganisms to grow faster (Abdel-Rahman et al., 2013; Chang et al., 1994).

The cassava is an important crop and basic food in many countries and due to industrial application, more quantity of bagasse was accumulated in the environment. The cassava bagasse contains 52% starch and also fibrous-rich residues. Rojan et al.(2005) clearly proved thatcassava waste was sacrificed and fermented by *L.* casei, which leads to the conversion of lactic acid production in a single step.

6.8.2.3 Recovery of LA

The quality and cost of LA depend on the recovery step, especially separation and purification. The cost of recovery consumes nearly half of the total production cost (Wasewar, 2005). Usage of further complex substrates with different compositions also creates a complication in the final product of LA, and theseparameters also play an important role in the purity and cost of LA. The separation of high-purity LA is achieved by the electrodialysis method. During the separation, frequent membrane blocking and deionization of broth areobserved, and so this technique ends up with a high-cost process (Komesu et al., 2017). Reactive extraction has been praised for high recovery and simple scale (Krzyżaniak et al., 2013). Good separation yields, reasonable costs and shorter process times havebeen reached by ion exchange chromatography than anyother downstream processes (Bishai et al., 2015), and high purity is achieved by anion and cation chromatography.

6.8.3 Chitosan

A linear cationic polysaccharide with a high molecular weight is chitosan. It is made up of randomly dispersed N-acetyl-D-glucosamine (acetylated unit) and -(1,4)-linked D-glucosamine (deacetylated unit) (Zargar et al., 2015; Islam et al., 2017).

6.8.3.1 Agro-wastes as Medium to Produce Chitosan

Leite et al. (2015) produced chitosan from sugarcane bagasse and corn steep liquor as substrate and fermentation by *Syncephalastrum racemosum*. Using sugarcane bagasse as carbon source and corn steep liquor as nitrogen source, the fungus was grown, and chitosan was extracted using alkali acid method. The viscosity and molecular weight were determined by vibrational spectroscopy, and the chitosan yield was about 23.5 mg/g. It clearly addressed that agricultural waste from the industries can be used to prepare a cost-effective medium to generate the biopolymer through fungal fermentation.

Instead of being utilized as filler in other materials, the chitosan-based substance is typically applied in biomedical and food applications. A catheter, a small tube that is inserted into a patient's body to cure diseases or perform surgery, can be coated with chitosan-based film in the field of biomedical applications. Chitosan is a substance that is placed on the outside of PET or polyethylene (PE) catheters because of its anti-adhesive and antibacterial properties (Lo et al., 2014; Muzzarelli, 1983). But before coating the catheter surface, chitosan must be heparinized to improve its blood compatibility and overcome its poor solubility. In application, the chitosan-heparin-coated catheter can therefore display high compatibility with the fluid and tissue around it in addition to thrombo-resistant qualities.

Chitosan is frequently used as a packaging material in the food industry (Nunes et al., 2018). There are a number of chitosan-based film types that have been researched for use in food packaging, including chitosan/polysaccharides-based films, chitosan/protein-based films, and chitosan/extracts-based films (Wang et al., 2018). Using grafting and cross-linking, chitosan is functionalized to get a perfect mechanical, antioxidant and antibacterial action. Liu et al.(2018) proved chitosan functionalization by grafting using 4-hexyloxyphenol, which has the ability to increase the radical scavenging capacity,that is, antioxidant activity.

6.9 OTHER AGRICULTURAL WASTES

In the current scenario of the world facing food scarcity, the research world is finding an alternative source to manufacture bioplastics,that is, plan to use the non-edible portion. The fruits skin like orange peel and banana peel, andvegetables like potato peel; cassava peels are used as a precursor to produce biopolymers. The most modern trend in the production of bioplastic films today is from polysaccharide residue feedstock, which is in great demand (Shah et al., 2021).

Pomegranate peel is one of the rich sources of bioactive compounds (Gumienna et al., 2016), which contains lignin 5.7%, hemicelluloses, cellulose 26.2% and pectin 27%. The polysaccharides were extracted and converted into simple sugars using the acid hydrolysis method, which is present in the pomegranate peel. Finally, it breaks down into hemicelluloses, celluloses and lignin compounds, and further, it acts as the primary source for the production of biopolymer carbohydrates present in the orange peel, and it can be used for the production of bioplastics. The accumulation of unprocessed peel createsmuchenvironmental pollution, and so conversion is very important in mutual way (Chozhavendhan et al., 2020).

6.10 APPLICATION OF AGRO-BASED BIOPLASTICS

Packaging of food, construction and farming are the places of important applications of agro-based bioplastics. This is due to the impact of quality properties like mechanical, chemical and physical of the bioplastics. Biopolymers with significant tensile strength/Young modulus are required for high-strength applications in construction and agriculture (Figure 6.5).

In packaging applications, the material's flexibility is one of the important factors. For example, tamarind fruit fibre hasa tensile strength of approximately 1360 MPa, resulting in the best mechanical characteristics ofbiopolymers produced from it and being replaceable to synthetic carbon (Binoj et al., 2017). In construction, biopolymer usage is enhanced by nourishing materials like carbon nanotubes, nanofibers and fillers from agro-wastes (Nagarajan et al., 2020). Agricultural shade nets and mulching films are produced using biobased polymers comprised of cellulose, starch, polyhydroxyalkanoates (PHA), bio-polyethylene and PLA(Briassoulis&Giannoulis, 2018; Mukherjee et al., 2019). Because commercial pesticides are so hazardous, using fewer of them has both ecological and financial advantages. Additionally, shade nets have better mechanical qualities than conventional low-density polyethylene films. The nets also assist in filtering UV light, which is detrimental to plant growth. These nets' tensile strength, mesh sizes, surface colour, and chemical makeup all have an impact on their commercial use. High-tensile strength shade nets have a longer usable life and can endure weather-related dangers including strong winds, sunshine, and hail (Mukherjee et al., 2019).

Due to the sustainability of biopolymers, it is used in food-packaging materials, and it is further enhanced using surface modification techniques by nano-fibrillated cellulose at different concentrations (Ilyas et al., 2019). Photobleaching was used to change the biopolymer structure of corn starch and blueberry powder, which helped develop intelligent foodpackaging solutions. The biofilms' luminance values

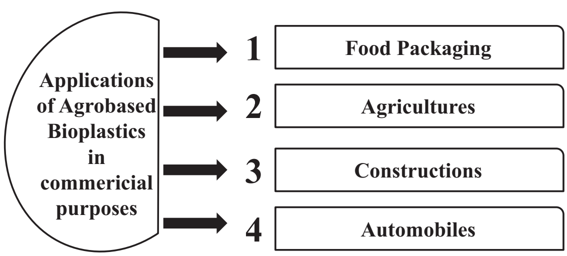

FIGURE 6.5 Application of agro-based bioplastics.

(surface colour), which were reduced by photobleaching, made them excellent colorimetric markers for the deterioration of packed food. In situations with acidic and basic pH levels, the biofilms, respectively, turned blue and red. Fermentation and an increase in pH are characteristics of food that havebeen packaged poorly. The human eye can distinguish the colour variations. Unfortunately, because they are unrelated to the shelf life of foods that contain various biomolecules including proteins, lipids, salt, and sugar, the intelligent pH detection findings are inconclusive (Luchese et al., 2017).

Biobased polymers' usable lives are influenced by how much UV radiation they are exposed to radiation that causes photo-oxidation heat that causes thermal deterioration, and the possibility of dissolution,both mechanical strength in water and high strength applications. There are numerous choices for end-of-life care for biodegradable materials, such as residential and commercial breakdown enzymatic depolymerization, catalytic recycling, chemical recycling, mechanical recycling, compostingandanaerobic digestion (Vroman & Tighzert, 2009).

6.11 CONCLUSION AND FUTURE PERSPECTIVES

The dependence on non-renewable resources has raised economic and environmental concerns, which have fuelled the development of the biopolymer sector over the years. The creation of novel bioplastics is one way to support the circular economy, which aims to reduce waste and resource consumption over time. Every nation needs the agro-industry because it is the cornerstone of economic growth. Trash that will pollute the environment has been produced during the processing and production processes in the agroindustrial sector.These agricultural wastes have emerged as enticing substitute sources for the creation of high-value products.As science and technology advanced, the uses of agricultural wastes in many industries, including the bioplastics industry, were identified.Future studies should concentrate on the characteristics of bioplastics made from agricultural waste. Future research on bioplastics nanocomposites and fibre-based composites is crucial to overcoming the inferior performance of bioplastics. The government should also play a part by boosting incentives for the creation and use of biopolymers from agricultural waste. The function of public-private partnerships should be addressed more carefully for the benefit of the bioplastics industry and the community as a whole.This chapter clearly revealed the state-of-the-art of agro-waste-based bioplastics and theircontributionto thebest economic growth of society. They also enhance a green environment as the agricultural wastes can be renewed into novel value-added products.

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