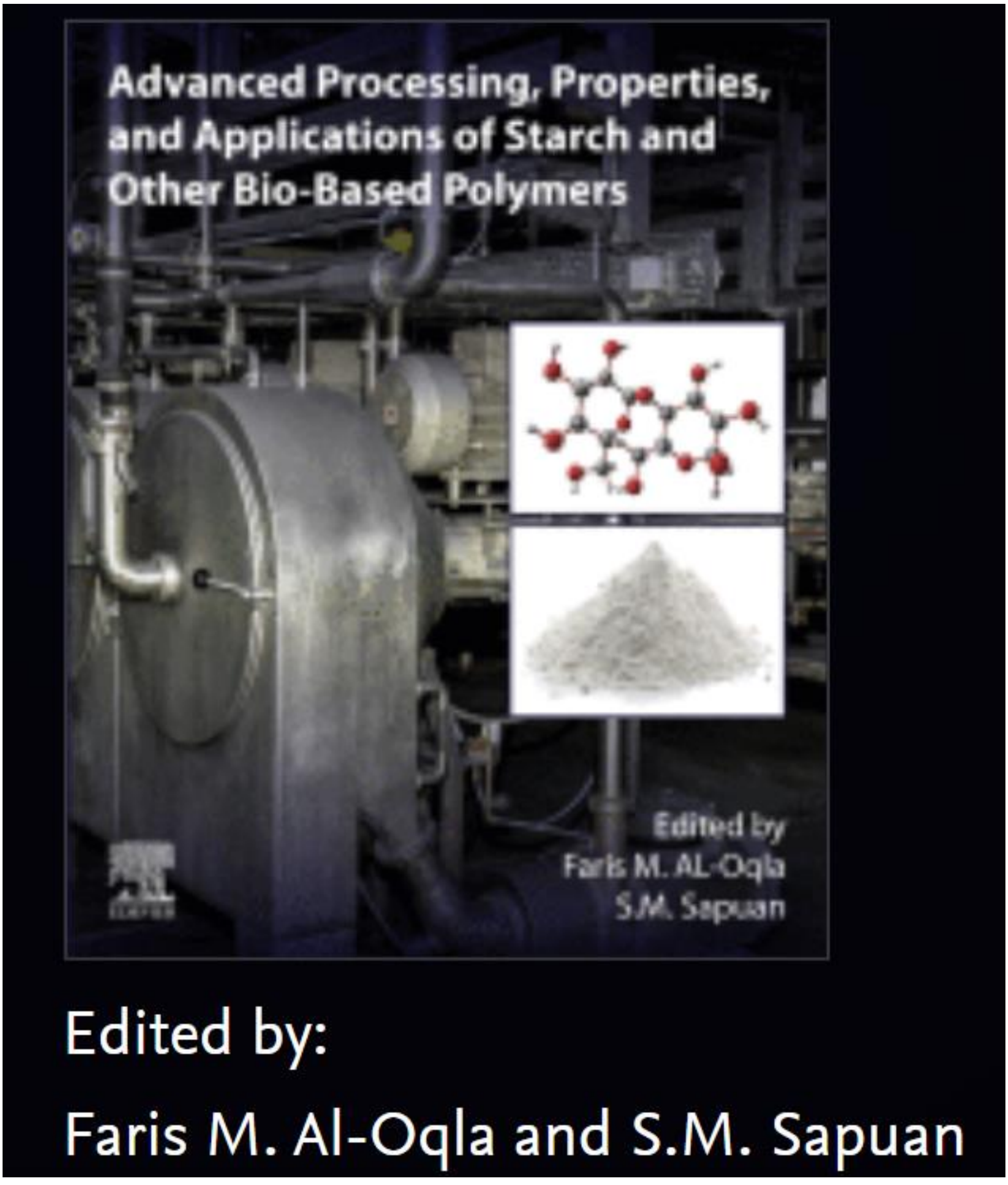
Properties and Characterization of PLA, PHA, and Other Types of Biopolymer Composites



CHAPTER Book

8

Advanced Processing, Properties, and Applications of Starch and Other Bio-Based Polymers

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Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library

ISBN: 978-0-12-819661-8

Publisher: Matthew Deans
Acquisitions Editor: Edward Payne
Editorial Project Manager: Charlotte Rowley
Production Project Manager: Kiruthika Govindaraju
Cover Designer: Alan Studholme

Typeset by TNQ Technologies

Full paper silahkan di https://drive.google.com/file/d/1gHDJtnfzZXd8JL7Ju8Ljv5FOB_rtONXt/view?usp=sharing

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CHAPTER 8

Properties and Characterization of PLA, PHA, and Other Types of Biopolymer Composites

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1 INTRODUCTION

The production of petroleum-based plastic had increased tremendously, reaching about 350 million tons annually (Garside, 2019). According to Rochman et al. (2013), the earth will accumulate with about 33 billion tons of plastic wastes by 2050, if current rates of consumption continue. Besides that, inappropriate usage and disposal of plastics waste would lead to substantial pollution of both terrestrial and marine ecosystems. The world produces about 350 million tons of plastic waste annually, and surprisingly, only 9% of this waste has been recycled (UNEP, 2018). Moreover, it had been estimated that each year at least 8 million tons of plastic waste go to the rivers and oceans, and some of them often decompose into small microplastics that end up stopping in our food chain (UNEP, 2018). Because of the environmental challenges aiming to reduce this environmental impact, many researchers have formulate eco-friendly and biodegradable composites polymer to replace conventional petroleum-based polymer.

Recently, many countries have banned petroleum-based plastics because of the huge volume of plastic waste that harmfully affects the ecosystem, wildlife, and environment (Aisyah et al., 2019; Asyraf et al., 2020; Atikah et al., 2019; Norizan et al., 2020; Nurazzi et al., 2019a). These nondegradable plastic are responsible for the "white pollution" worldwide. The "white pollution," including plastic bags, plastic bottles, plastic silverware, and other materials that are made from the plastic, kills the wildlife, marine life, and avifauna and degrades the quality and features of the environment on the Mother Nature (Thiagamani et al., 2019). Remarkably, Malaysia is the foremost country in Southeast Asia region to take courageous act to confront "white pollution." The Government of Malaysia has broadcasted that the government will ban single-use plastic by year of 2030 (UNEP, 2018). Although Malaysia is a bit behind when it comes to enacting against single-use plastics, nevertheless according to New Strait Times, Federal Territories of Malaysia has announced that from March 2019, a pollution charge of 20 cent imposed for a single plastic bag. Therefore, customers will either have to pay 20 cent for a reusable bag or bring their own bags. Besides Malaysia, others countries such as Kenya, China, Rwanda, Uganda, Ireland, South Africa, Morocco, Taiwan, India, France, and Canada have already forbid and eliminated completely the use of single-use plastic and plastic bags.

Therefore, in order to cater this problems, biodegradable polymers were introduced. Biodegradable polymers are one of the potential solutions to the problems associated with discarded wastes (Abral et al., 2020a,b; 2019a; Atiqah et al., 2019; Ilyas et al., 2018, 2017; Nurazzi et al., 2019b). This is due to their fast degradation by the action of naturally occurring microorganisms in the environment (Ilyas et al., 2018a). Biodegradable polymer can be produced via (1) bio-based (i.e., polyhydroxyalkanoates [PHA], starch, protein, polylactic acid [PLA], chitin, chitosan, polybutylene succinate [PBS], and cellulosics) and (2) fossil- or petroleum-based (i.e., polycaprolactone [PCL], poly(vinyl alcohol), and poly(butylene adipate-co-terephthalate) materials.

Generally, polymer is made up of long chain of polymer with many repeated subunits. Both man-made

 https://doi.org/10.1016/B978-0-12-819661-8.00008-1

(synthetic) and natural polymers play important and ubiquitous roles in daily life. This is because of their various unique properties (Ilyas et al., 2018a). They are made by the process of condensation and addition polymerization reactions. They can be categorized either as thermosetting or thermoplastic polymers. "Bio-based plastic" can be defined as a plastic that are made from natural resources and it is renewable, whereas "biodegradable plastic" is referred on how the plastics behave at end of its life. The illustrations of bioplastic is displayed in Fig. 8.1.

Biodegradable plastic is a material that is decomposed naturally when introduced in the environment by the action of living organisms, usually microorganisms. It is eco-friendly compared with conventional plastics. Besides that, this plastic is commonly produced via microorganism, renewable raw materials, petrochemicals, or combination of all three. There are a lot of materials that can be used to make biodegradable and bio-based plastics such as plants, starches (cassava, corn, potato, sugar palm, yam bean, pea, wheat tapioca, bengkuang), peels from citrus fruits, and corn oil (Atikah et al., 2019; Halimatul et al., 2019a,b; Jumaidin et al., 2019a–c; Syafri et al., 2019). Biodegradable and bio-based plastic offer a material that is made from natural resources, therefore the risk of breaking down these material are much fewer compared with conventional petroleum-based plastic. Fig. 8.2 shows some of the list of the advantages and disadvantages of utilizing biodegradable plastic.

Biodegradable plastic is often reflected as a savior product. Shifting to these materials would decrease the levels of greenhouse gas emission, reduce carbon dioxide levels, reduce energy of manufacturing, reduce amount of waste produced, and create new plastic industries. However, there is also the potential for biodegradable plastic to create more pollution. This is because biodegradable plastic is difficult to be decomposed in ocean water like it would during composting in soil. This plastic will either float on the ocean or river surface like other conventional plastic or more worse it create microplastic that is harmful to marine life, sea life, or ocean life. Therefore, shifting to this biodegradable plastic is not a final solution that will resolve our pollution problems. More research must be done to develop total biodegradable plastic that can be degraded fully in every condition. The advantages and disadvantages of biodegradable plastic provide opportunity to reduce human dependence in fossil fuels especially in reliance on crude oil or petroleum. There are several types of biodegradable and bio-based polymer such as PHA, PLA, starch, protein, chitin, chitosan, and PBS (Azammi et al., 2020). Therefore, this chapter focuses on providing an overview of recent advancements on biodegradable bio-based polymer for various application.

2 POLYHYDROXYALKANOATES

PHA are a kind of degradable plastics. It has good environmental effects compared with petroleum-based

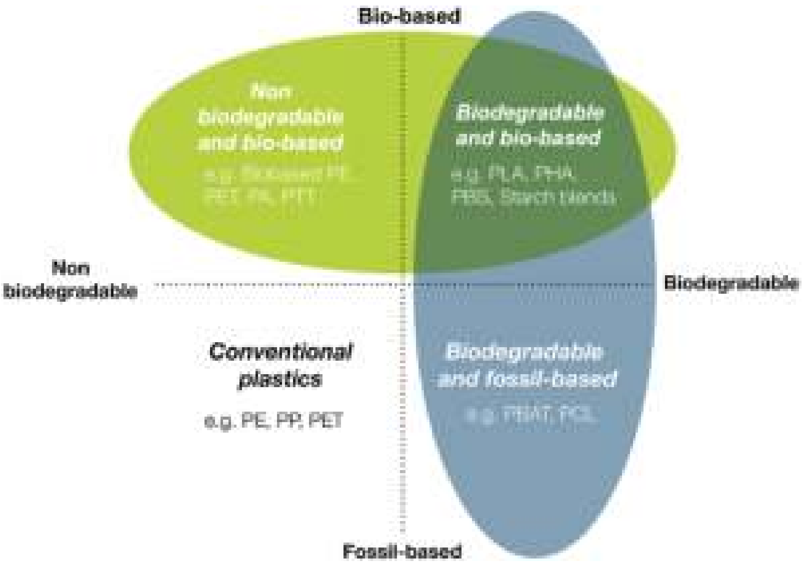

FIG. 8.1 Conventional petroleum-based plastics and bioplastics are that made up of biodegradable polymers (Ilyas and Sapuan, 2020).

Advantages

- Can be broken down by naturally occurring microorganism
- Reduces greenhouse gas emission levels
- Reduces carbon dioxide levels
- Does not release other harmful products after disposal
- Uses low energy during the production cycle
- Reduces the amount of waste we produce
- Current use of petroleum can be channeled to other needs
- Can mix and blend with conventional plastic
- Could create new export industries
- Could establish a new business opportunity and marketing platform
- Can degrade faster under certain conditions

Disadvantages

- Disposal of bioplastic waste must be through certain procedures
- Requires the some certain environmental conditions such as UV light, temperature and humidity) to associated with their disposal
- The costs of pesticides and herbicides are not taken into account during the manufacturing of biodegradable plastic
- The utilization of biodegradable plastics would reduce the number of plastic that can be recycling due to their limited properties
- High capital cost
- Requires croplands to produce items
- Some of the bioplastics only reduce their size to microsize plastic during decompostion process, but this does not solve the current ocean pollution problems, besides contaminated microplastics could expose marine organism to high concentrations of toxins
- May produce methane in landfills

FIG. 8.2 Advantages and disadvantages of biodegradable plastics.

polymer. PHA is a natural biopolymer material developed rapidly in recent 20 years. PHA are polyesters that were synthesized in nature by many microorganisms, including bacterial fermentation of lipids and sugars.

PHA has good mechanical, thermal processing, biodegradability, and biocompatibility properties. It can be used in agricultural materials, biomedical materials, and packaging applications. Recently, this polymer has attract huge attention in field of biomaterials.

Besides that, the blending polymer of starch and aliphatic polyester from sustainable and renewable resources to produce biodegradable plastics such as garbage bags and other products has been successfully studied and applied in American and European countries. One of the company named Novamont in Novara, Italy, had promoted a bioeconomy model based on the efficient use of resources and on territorial regeneration (Sahay and Ierapetritou, 2009). This company sets up biorefineries for the production of bioplastics and bioproducts of renewable resources conceived to protect environment, ecology, and wildlife. In 2018, Novamont had announced the opening of a revamped Mater-Biopolymer plant south of Rome to produce MATER-BI. This plant significantly boosting production capacity from 120,000 tons per year to 150,000. Remarkably, MATER-BI is widely used in Europe and the United States.

Polyhydroxyalkyl fatty acid esters (PHA) are biosynthetic polyesters consisting of a series of different repetitive unit structures. PHA has many interesting properties and has been utilized in many applications such as medical applications, fishing lines, and plastics bag. The biosynthesis of PHA monomer depends on many aspects, including the types of carbon sources on which biological growth depends, the types of metabolic pathways through which organisms convert these carbon sources into PHA monomers, and the substrate specificity of enzymes involved in PHA synthesis (Pérez-Arauz et al., 2019).

2.1 Properties of Polyhydroxyalkanoates

PHA is a kind of thermoplastic material with high degree of result. Its physical properties and chemical structure are basically similar to polypropylene (PP) and polyethylene (PE), and it is capable of drawing, pressing film, injection molding, etc. PHA is a kind of intracellular carbon source and energy storage, which can be naturally decomposed and utilized by many microorganisms and is biodegradable.

Soil burial experiments showed that PHA films with thickness of 0.07 mm could be degraded basically in about 6 weeks. The intracellular degradation of PHA was mainly through the formation of monomers or dimers by PHA depolymerase. There were two mechanisms of extracellular degradation, one was the automatic hydrolysis of melting bonds without supervision, and the other was decomposed by depolymerization of extracellular PHA. For example, as shown by Mergaert et al., 295 microorganisms have been found to degrade PHA in soil. In addition to the main characteristics of biodegradability, PHA has special properties such as bio-PHAe transport, optical activity, piezoelectricity, foam resistance, low permeability, etc. It can be widely used in industry, agriculture, medicine, scientific research, and other fields (Lu et al., 2009). In the PHA family, more than 90 different monomers have been discovered, except for a small number of 4-hydroxybutyric acid, 4-hydroxyvaleric acid, and 5-hydroxyvaleric acid, most of which are 3HA. At most, the fermentation mechanism and its properties are well known.

2.2 Advantages of Polyhydroxyalkanoates

PHA (and bioplastics in common) are exceptionally appealing materials for three essential reasons: they can be made from renewable sources, they can biodegrade, and they are biocompatible. To the primary point, it is exceptionally energizing that researchers are finding ways to gather and utilize fabric from sources like microbes amalgamation (PHA) and corn or sugarcane (other bioplastics like PLA). Already, crops had to be redirected for the production of bioplastics, but within the final decade or so, there has been a center on utilizing squander materials (such as banana peels, potato peelings, etc.) to deliver bioplastics instep. By utilizing squander items, utilization of rare assets can be maximized.

Biodegradability is the other key viewpoint that creates PHA an awfully promising material. Environmental contamination could be a hot subject with vital suggestions; ordinary petrochemical-based plastics have been at the exceptionally center of the controversy, fundamentally since they are so broad and do not degrade effectively. For occasion, pictures of marine creatures choked by or ingesting different plastics show the stark reality of contamination. Of course, fossil fuel-based plastics have done much to move forward the material lives of people, but when it comes to contamination, modern developments in biodegradability are exceptionally welcome.

Since PHA are biocompatible (which implies not destructive to living tissue), they can and have been used in an assortment of therapeutic and surgical applications. Looking forward, the potential moreover exists that PHA will be included in "wearable" inner innovation applications.

PHA can reduce the landfill needed to bury the plastic waste as the period time needed for PHA to biodegrade is fast and reliable, which reduces the impact to environment. Besides, biopolymers can decrease the natural affect derived from plastic waste transfer due to the truth that the biodegradation time for biopolymers within the land surface beneath standard conditions is roughly 2 months (Hassan et al., 2013).

PHA have the advantages to biodegrade in most of the situation, not only on land surface but also in water area due to the special process undergone during the biodegradation process. PHA can be biodegraded under both anaerobic and aerobic conditions by PHA degraders as shown in most situation, including the marine environment (Shah et al., 2008).

2.3 Application of Polyhydroxyalkanoates

Bacterial plastics have gained a very high attention worldwide and globally as the better choice in packaging materials. The applications include in medical devices, skin care, personal hygiene products, plastic packaging, and utilized in agricultural field as mulching films. It is an alternative option for conventional plastics that are being used in agriculture field, which are nonbiodegradable and nonenvironment friendly. This bacterial plastics are the better substitution for those examples mentioned previously because these conventional plastic are single-use application and the demand amounts are enormous, thus creating a lot of plastic waste. According to Chen (2010), the application of PHA is not only limited to bioplastics application, however, PHA have also been make full use as implant biomaterials, biofuels, fine chemicals, medicines, and for regulating bacterial metabolism as well as enhancing the quality of industrial microorganisms.

The scope of application was made possible by further chemically modifying the PHA's functional groups. The utilization of PHA in various industries has grown considerably wide. Currently, aluminum is used as cover for cupboard to prevent water from entering the product. Hence, to overcome this problem, PHA latex can be utilized to cover cardboard to make the surface of product water-resistant. Besides that, only small amount of PHA is required for this purpose, and thus it works out to be cost-effective alternative (Patricia et al., 2007).

Nonetheless, PHA is also extensively use in the tissue engineering. Tissue engineering involves the use of a tissue scaffold for the formation of new viable tissue for a medical purpose. Therefore, suitable material for this application must have properties such as support cell growth, allow tissue ingrowth, guide and organize the cells, degrade to nontoxic products, and biocompatibility. Thus, according to these criteria, PHA is seem completely fit into these criteria and make it the best candidate as the suitable material to be used in tissue engineering application.

Furthermore, PHA also can be utilized in controlled drug release systems. The capability of this material to work with a suitable host response and biodegradability properties make it useful for drug delivery in the medical field. Besides that, many researches have been conducted and stated that various variety of monomers can be added into PHA for modification. These modification would result in numerous changes of physical properties that range from strong elastomers to highly crystalline materials. The rate of decomposition can be indirectly controlled by precisely controlling the monomer composition of PHA. Catalyst reaction of the enzymatic degradation is normally done by bacterial PHA depolymerase.

Metabolix, a US-based company, blend P(3HB) and poly(3-hydroxyoctanoate) to produce a new compound of PHA and marketed their product in the market. This newly formed PHA compound is an elastomer that has been ratified by the Food and Drug Administration for usage as food additives. This example shows that the range of PHA application has been expanded widely as they could even found in the food industries.

Following by the application in food additive, the application of PHA can be found in the electronic industries as well. This function is possible due to the PHA piezoelectric nature. The electronic components or parts that can be produced by PHA are stretch and acceleration measuring instruments, shock wave sensors, gas lighters, lighters, material testing, pressure sensors for keyboards, oscillators: for atomization of liquids and ultrasonic therapy, loudspeakers, headphones, and acoustics: sound pressure measuring instruments, ultrasonic detectors, and microphone.

Last but not least, polystyrene (PS) waste was renowned as the waste materials that takes the longest degradation time or might be nondegradable. However, with the advanced scientific exploration, researchers were able to devise a novel way to alter the abundant PS waste into PHA biopolymer using combination of pyrolysis. This process is cost-effective and efficient and can be one of the ways to optimize the use of PS residues.

3 POLYLACTIC ACID

World issues such as environmental, economic, and health issues have been constantly pushing scientists, researchers, and manufacturers to slowly replace the extensive use of plastics in the current world. Most plastics produced today are made from nonrenewable resources such as petroleum. Unlike any other plastics, PLA is made up from renewable resources such as corn starch or sugar cane (Siakeng et al., 2019). PLA is known as bioplastic because it is obtained from biomass. Not only that PLA is biodegradable, it also has attributes like PS, PE, or PP. Due to its similar production process, it can be produced easily from the existing production plant for petrochemical industry plastics. This advantage makes it cost effective to be utilized. PLA is mainly produced through condensation and polymerization processes. Ring-opening polymerization process is a procedure that uses metal catalyst mix with lactide to form a bigger PLA molecules. Similarly, the condensation process goes through the same procedure with different temperature and produce different by-products (Singhvi et al., 2019). There are few types of PLA, e.g., racemic PLLA, regular PPLA, PDLA, and PDLLA. All of them are having different characteristics yet similar because they are derived from renewable sources. PLA is a thermoplastic polyester which means that it can be heated to their melting point at around 150−160°C, cooled, and heated again without any degradation. In contrast, the thermoset plastic can be heated only once and it is irreversible. Due to its characteristics, PLA has been the most studied and utilized biodegradable plastic in the human history. It is replacing conventional petrochemical-based polymers slowly and becomes the leading biomaterial for medical application as well as in other plastic industries (Farah et al., 2016).

3.1 Advantages of Polylactic Acid

PLA is tremendously used in research and daily life as biocompatible polymer due to properties without toxic or carcinogenic effects for human body (Rasal et al., 2010). For quite a long time, we have been cautioned of the hazardous synthetic substances that escaped when common plastics are burned. In biological perspective, PLA plastics do not develop these poisonous gas if ended up in the event of burning instead of finding their path to a composting facility operate in large scale.

Most of the polymers that exist nowadays are derived from nonrenewable resources especially petrochemical, which are just accessible in limited quantity all through the world. In the end, these fossil resources will be used up. Production of synthetic polymers, as well as to get rid of it by burning, will create a lot of CO_2, which contributes to the global warming (Pang et al., 2010).

PLA, which is produced from corn, is a resource that can be restored every year (Singhvi et al., 2019). PLA are getting more attention commercially since they are produced from corn-based starch, sequester critical amounts of CO_2 in respect to petrochemical-based materials, save energy, and degrade in a short time. Researchers have shown that PLA demonstrates lower fossil resources utilization, which reduces the risk of summer smog and global warming.

PLA will bring a lot of benefits such as its preparation from lactide monomer which can get from a renewable source in agriculture field (Gewin, 2003; Sawyer, 2003), low quantities of CO_2 used up (Dorgan et al., 2001), the contribution in reducing amount of landfill and developing economies of farm, and lastly better mechanical properties compared to PS and PET (Auras et al., 2005).

3.2 Disadvantages of Polylactic Acid

Table 8.1 give a summary on the degradation rate of some synthetic polyesters. It show that PLA is slower than PGA, PLGA, and PCLA copolymers in term of degradation rate. The reason behind this condition is the poor properties that make the water diffusion difficult to the semicrystallinity of PLA.

TABLE 8.1
Biodegradation Rate of Some Polyesters (Ikada and Tsuji, 2000; Zhu et al., 1991).

Polymers	Molecular Mass (kDa)	Degradation Rate
PLLA	100–300	(SC) 50% in 1–2 years
PGA	–	(C) 100% in 2–3 months
PLGA	40–100	(A) 100% in 50–100 years
PCL	40–80	(SC) 50% in 4 years
PCLA	100–500	(A) 100% in 3–12 months
PTMC	14	(SC) 9% in 30 weeks

To some certain extent, despite the fact that PLA is biodegradable, the duration taken will be so long. As indicated by Elizabeth (2006), PLA may well separate into its constituent parts, carbon dioxide and water in a controlled composting condition, that is, increase the surrounding temperature to 140°F. In any case, it will take much more time in a fertilizer container or in a landfill stuffed so firmly that no light and little oxygen are accessible to aid the procedure.

It is regretting to say that, most PLA plastic will not break down into natural components in any composting pile appearing in courtyard. Rather, these items should be transported to a commercial composting facility. In any case, as the business develops, we trust that the facility for commercial composting will tag along. Discarding PLA plastic items in a landfill would be considered as a suicide alternative.

3.3 Application of Polylactic Acid

There are three main applications for PLA plastics, which are domestic, medical, and packaging and 3D printing applications. Table 8.2 shows the applications of PLA and its usages.

4 STARCH

Starch-based biopolymer films have been extensively utilized in medicine as well as food packaging application, in which the biofilm should be edible in many cases, such as applications in medicine capsules, candy wrappers, etc. This type of biofilm has a potential to be used for controlling water permeability, as a barrier for volatile compounds and gases, and to maintain the food freshness. However, starch-based biopolymer has poor mechanical properties and high water vapor permeability. To overcome this drawback, starch-based biopolymers are (1) blend with other polymers, (2) reinforced with plasticizer, particle, or fiber fillers, or (3) modified to starch structure (Ilyas et al., 2020a,b, 2019a–d, 2018a–d; Sanyang et al., 2018). Nevertheless, the reinforcement of filler or plasticizer has some problems related to safety issues. Therefore, the selection of filler, plasticizer, polymer blend, and chemical used to modified starch must be nonallergic, nontoxic, fully biodegradable, and digestible and can be consumed by living things.

4.1 Properties of Starch

Physically, most native starches are semicrystalline, having a crystallinity of about 20%–45% (Abral et al., 2019b). The short-branched chains in the amylopectin

TABLE 8.2
The Application of PLA Plastics (Jamshidian et al., 2010).

Number	Applications	Usages
1	Domestics	Plates and saucers, cups, cutlery, fruit juices, fresh water, sports drinks, cold drink cups, transparent food containers, foodware, dairy containers, jelly and jam container, and edible oils container.
2	Medical	Medical devices such as plates, rods, pins, and screws.
3	Packaging	Vegetable bags, candy twist wrap, lidding film, salad, blister packaging, window envelope film, label film, shrink wrap material, and other packaging applications.
4	FDM machines (3D printing)	3D printable filament, lost PLA casting for molten metal, and other 3D printing medical device prototypes (both biodegradable and permanent).

are the main crystalline component in starch granular. Crystalline regions exist in the form of double helices with a length of ~5 nm. Besides that, the amylopectin segments in the crystalline regions are all parallel to the axis of the large helix. The molecular weight of amylose is about 100 times lower than that of amylopectin. Moreover, the ratio of amylose to amylopectin much depends on the age and source of the starch. In addition, the ratio of amylose and amylopectin can also be controlled by the extraction process method used. Starch granules also contain small amounts of lipids and proteins. Fig. 8.3 shows the chemical structures and physical diagram illustration of amylopectin starch and amylose starch (Generalic, 2019). Moreover, thermoplastic starch (TPS) is formed by disrupting the ordered structures within the starch molecular. Heating process is required along with shear force to disrupt the starch granules. This shear forced and heating process would cause swelling and nonirreversible transition of amorphous regions in the presence of plasticizer, under certain condition (Sanyang et al., 2016). Table 8.3 shows the chemical composition of commercial starches. Besides that, from Table 8.4, it can be observed that the highest amylose content is sugar palm starch (SPS). Table 8.5 shows the SPS properties in comparison with sago starch. The mechanical properties of SPS biofilm was observed higher compared with sago starch biofilm. Therefore, SPS biofilms have higher potential to be utilized as bio-based packaging.

4.2 Advantages and Disadvantages of Starch Biopolymer

The development of novel starch-based polymer materials using renewable resources became hot topic among the researchers to overcome the environmental problems caused by plastic wastes. Starch can be extracted from sugar palm tree, tapioca, wheat, tapioca, potato, cassava, bengkuang, and maize (Jumaidin et al., 2019a,b, 2020). Generally, such material is stored in plants tissues as one-way carbohydrates. It is made up of glucose and can be attained by melting starch. However, this polymer is not available in animal tissues. Starch possess several advantages such as abundance, renewability, easy availability, biodegradability, ease process, and cheap. Native starch-based biopolymer possess many disadvantages, such as high thermal degradation rates, low mechanical properties, high water-barrier properties and processability (Hazrol et al., 2020; Nazrin et al., 2020). The disadvantages of starch-based biopolymer are listed in Fig. 8.4. Current technique that is being used to process starch nowadays is solution technique. Solution casting technique is the easiest and most widely utilized at laboratory scale compared with other method such as hot press. However, this technique cannot be conducted at large-industrial scale as it encompasses too long drying time processed. Therefore, in order to overcome this problem, the fabrication of starch-based polymer by thermoplastic treatments (reactive extrusion, foaming extrusion, film/sheet extrusion, and injection molding) could be considered.

4.3 Application of Starch Biopolymer

Bio-based and biodegradable starch-based biopolymers have an extensive range of applications such as mulching film horticultural crops, drop ceiling tiles, pharmaceutical, biomedical, corrugated board adhesives, paper, horticulture, agriculture, consumer electronics, automotive, textiles, and packaging (Spaccini et al., 2016; Tan et al., 2016). Table 8.6 summarized the starch-based biopolymer, its manufacturing technique, and applications.

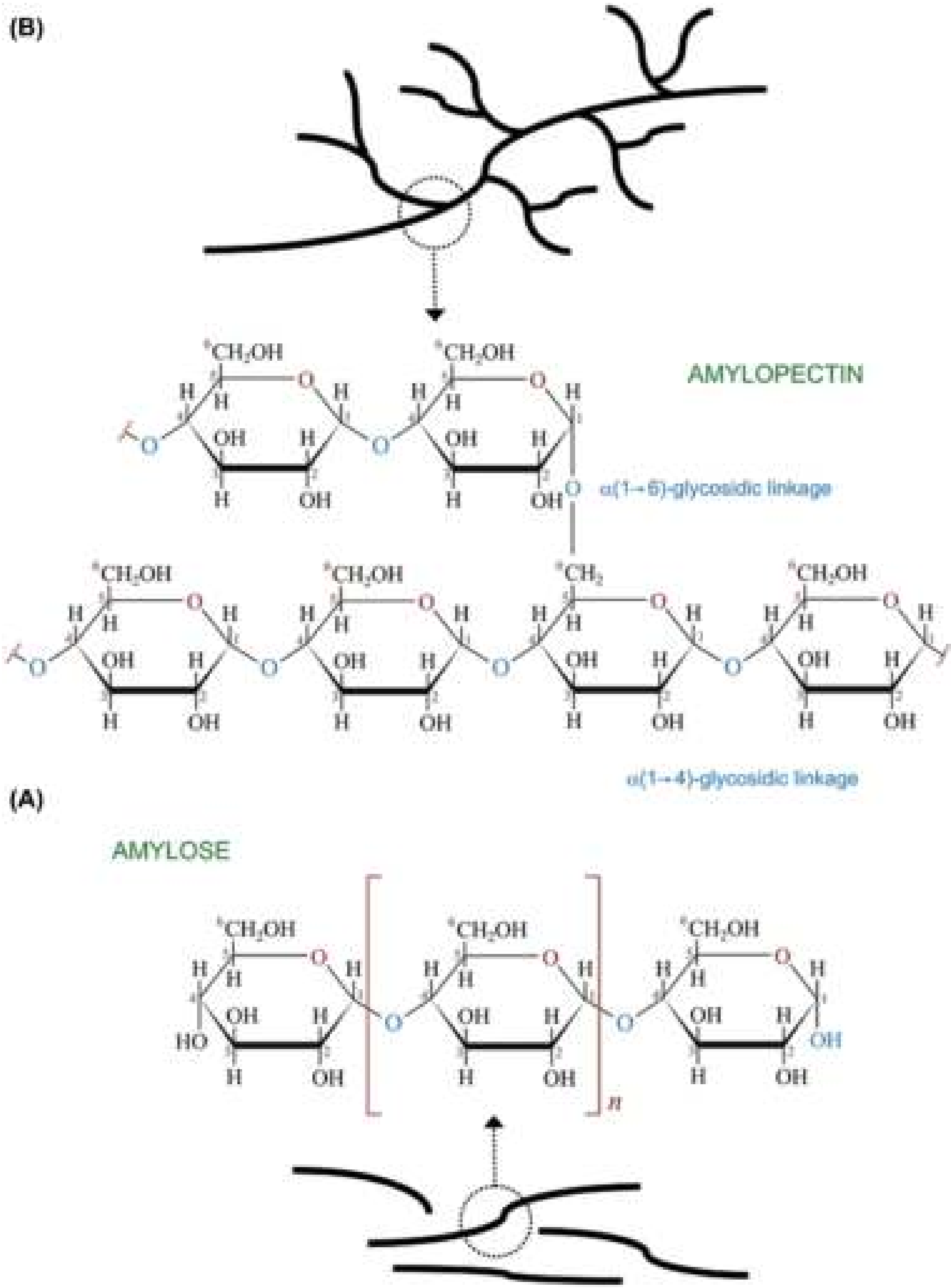

FIG. 8.3 Chemical structures and physical schematic representation of **(A)** amylose starch and **(B)** amylopectin starch.

TABLE 8.3
The Chemical Composition of Commercial Starches (Sanyang et al., 2016).

Starch	Density	Ash (%)	Amylose (%)	Water Content (%)
Wheat	1.44	0.2	26–27	13
Tapioca	1.446 –1.461	0.2	17	13
Maize	1.5	0.1	26–28	12–13
Potato	1.54 –1.55	0.4	20–25	18–19
Sago	–	0.2	24–27	10–20
Sugar palm starch	1.54	0.2	37.60	15

5 PROTEIN

5.1 Properties of Protein Biopolymer

Protein is considered as one of the most plentiful biological macromolecules in cells, occurring in an extensive variety of species and ranging in size from relatively small peptides to polymers with high molar mass. These molecules exhibit diverse biological functions (Durán et al., 2011), providing structure or biological activity in animals or plants. Besides that, proteins are well-known and compared with other macromolecules due to their structure that is based on approximately 20 amino acid monomers, rather than just a few or even one monomer, such as glucose in the case of cellulose and starch. Most proteins contain 100–500 amino acid residues (Fennema, 1985; Haghpanah et al., 2009).

The functional variety of proteins basically arises from their chemical structure. Depending on the sequential order of the amino acids, the protein will

TABLE 8.4
Properties of Sugar Palm Starch in Comparison With Sago Starch (Adawiyah et al., 2013).

Characterization	Parameters	Sugar Palm Starch	Sago Starch
Chemical composition	Amylose (%w/w) Fat (%w/w)	37.6 ± 1.46 0.27 ± 0.00	36.6 ± 1.55 0.24 ± 0.00
	Protein (%w/w)	0.10 ± 0.00	0.08 ± 0.00
	Moisture (%w/w)	9.03 ± 0.00	9.17 ± 0.00
	Ash (%w/w)	0.20 ± 0.00	0.16 ± 0.00
Gelatinization properties	Onset temperature (T_O) (°C) Peak temperature (T_P) (°C)	63.0 ± 0.12 67.7 ± 0.07	58.1 ± 0.28 67.3 ± 0.21
	Conclusion temperature (T_C) (°C)	74.6 ± 0.42	79.4 ± 0.88
	Range (T_C–T_O) (°C)	11.6 ± 0.49	21.3 ± 0.79
	ΔH (J/g)	15.4 ± 0.25	16.4 ± 0.24
Mechanical properties	Stress at 10% strain (kPa) Stress at shoulder point (kPa)	0.61 ± 0.10 23.0 ± 3.65	0.41 ± 0.04 15.5 ± 0.96
	Strain at shoulder point (%)	54.4 ± 3.54	59.1 ± 2.28
	Working until shoulder point (N mm)	20.2 ± 1.80	14.1 ± 0.82
	Breaking stress (kPa)	29.8 ± 2.64	–
	Breaking strain (%)	60.1 ± 2.61	–
	Work until breaking point (N mm)	29.6 ± 2.45	–
	Compressive force after breaking at 70% strain (N)	8.77 ± 0.59	9.97 ± 1.11
	Compressive force at 90% strain (N)	43.8 ± 2.34	44.0 ± 3.89
	Working until 90% strain (N mm)	108 ± 6.11	90.3 ± 8.37
	Adhesive force (N)	−3.64 ± 0.96	−8.99 ± 1.57

TABLE 8.5
Mechanical Properties of Starch-Based Biopolymer.

Film	Tensile Strength (TS, MPa)	Elasticity Modulus (EM, MPa)	Strain at Break (ε, %)	Year	References
Maize starch	0.24–20	51–315	–	2001	Anglès and Dufresne (2001)
Wheat starch	2.5–7.8	36–301	–	2005	Lu et al. (2005)
Potato starch	3	45	47	2006	Thunwall et al. (2006)
Rice starch	3.2	–	–	2006	Mehyar and Han (2006)
Pea starch	4.2	–	–	2006	Mehyar and Han (2006)
Amaranthus cruentus flour	0.8–3.0	–	74.2–620	2006	Colla et al. (2006)
Pea starch	1.4–5.8	8–98	38–51	2006	Zhang and Han (2006)
Maize starch	1–15	11–320	–	2006	Angellier et al. (2006)
Wheat starch	2.8–6.9	56–480	–	2006	Lu (2006)
Potato starch	13.7	460	–	2007	Kvien et al. (2007)
Corn starch	3	–	20	2008	Dai et al. (2008)
Pea starch	3.9–11.5	31.9–823.9	–	2008	Cao et al. (2008a,b)
Pea starch	3.9–11.9	31.9–498.2	–	2008	Cao et al. (2008a,b)
Maize starch	42	208–838	–	2008	Mathew et al. (2008)
Cassava	1.4–1.6	5–21	30–101	2009	Muller et al. (2009)
Cassava starch	4.8	84.3	–	2009	Teixeira et al. (2009)
Mango puree	8.76	322.05	–	2009	Azeredo et al. (2009)
Maize starch	6.75	220	–	2010	Kaushik et al. (2010)
Pea starch	2.5–12	20.4–210.3	–	2010	Liu et al. (2010)
Wheat starch	3.15–10.98	–	–	2010	Chang et al. (2010)
Corn starch	2.5–3.6	21–533	48–63	2011	Fu et al. (2011)
Rice starch	1.6–11	21–533	3–60	2011	Dias et al. (2011)
Maize starch	0.35	3.12	–	2011	Teixera et al. (2011)
Potato starch	–	460	–	2012	Chen et al. (2012)
Potato starch	17.5	1317.0	–	2013	Hietale et al. (2013)
Potato starch	5.01	160	–	2014	Nasri-Nasrabadi (2014)
Maize starch	2.35	53.6	–	2014	Karimi et al. (2014)
Maize starch	17.4	520	–	2014	Slavutsky and Bertuzzi (2014)
Cush-cush yam starch	1.88	13.9	19	2015	Gutiérrez et al. (2015)
Corn starch	38.0	141.0	–	2015	Babaee et al. (2015)
Potato starch	4.93	–	–	2016	Noshirvani et al. (2016)

Corn starch	11.2	12.4	–	2017	Llanos and Tadini (2018)
Sugar palm starch	4.8	59.97	38.10	2018	Ilyas et al. (2018a)
Yam bean starch	11.47	443	–	2018	Asrofi et al. (2018a)
Sugar palm Starch	11.5	178	–	2018	Ilyas et al. (2018a)
Tapioca starch	5.8	403	–	2018	Asrofi et al. (2018b)
Tapioca starch	12.48	479.8	–	2018	Syafri et al. (2018)
Sugar Palm Starch	10.68	121.26	–	2019	Ilyas et al. (2019c)
Bengkuang starch	–	–	–	2019	Syafri et al. (2019)

assume different structures along the polymer chain, based on disulfide cross-link interactions among the amino acid units, hydrophobic, electrostatic, hydrogen bonding, and van der Waals (Fennema, 1985). There are approximately billions of proteins with distinctive properties that can be produced by altering the chain length of polypeptides, the type and ratio of amino acids, and sequence of amino acid. Usually, oilseeds, milk, vegetables, cereals, eggs, and meats (including poultry and fish) have been the main sources of food proteins. According to Fennema (1985), the functional properties of proteins in foods are related to their structural and other physicochemical characteristics. Besides that, the structures of proteins can be altered by various chemical and physical processes such as metal ions, acids and alkalis, lipid interfaces, irradiation, pressure, mechanical treatment, and heat treatment (Fennema, 1985). Such agents have the capacity to change the proteins structures and affect their functional properties. In films development, these modifications are often used in the formation process to optimize proteins configuration and interactions, resulting in better film properties.

A wide variety of proteins from animal/vegetable sources can be used to produce films, as shown in Table 8.7. In addition to the use of proteins for films production, researchers are focusing on the study of some strategies to improve their performance and to provide bioactive properties. In the group of animal proteins, the most used are caseins, whey protein, collagen, gelatin, myofibrillar proteins, and egg proteins, and among the vegetable proteins, the most used are soy protein, gluten, and zein (Mhd Haniffa et al., 2016; Pérez-Gago and Rhim, 2014).

In addition, casein-based films and biomaterials obtained from caseinate can be found in many applications such as in mulching films, in coatings for vegetables and fruits, in edible films, and in packaging

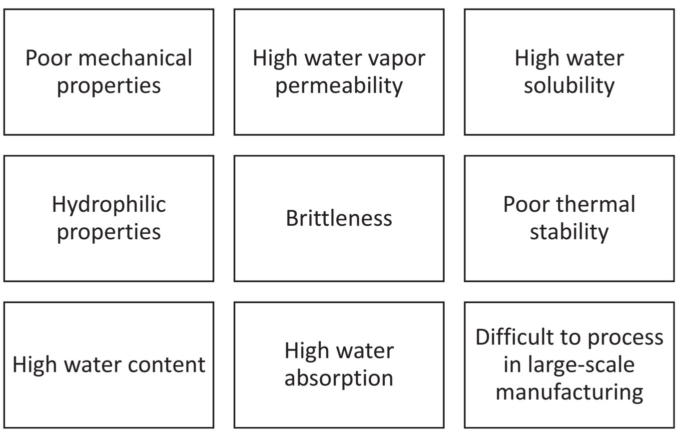

FIG. 8.4 Disadvantages of starch-based biopolymer.

TABLE 8.6
Starch-Based Biopolymer, Its Manufacturing Technique, and Applications.

Polymer Component	Manufacturing Techniques	Applications	References
Plasticized starch	Solution casting	Transparent materials	Nasseri and Mohammadi (2014)
Starch	Blending, solution casting	Air permeable, resistant, surface-sized paper, food packaging	Slavutsky and Bertuzzi (2014) and Yang et al. (2014)
Starch	Solution casting	Food packaging	Liu et al. (2010)
Cassava starch	Solution casting	Food packaging	Teixeira et al. (2009)
Sugar palm starch	Solution casting	Food packaging	Ilyas et al. (2018e)
Sugar palm starch	Solution casting	Food packaging	Ilyas et al. (2018b)
Sugar palm starch	Solution casting	Food packaging	Atikah et al. (2019) and Ilyas et al. (2018e)
Wheat starch	Solution casting	Food packaging	Lu et al. (2006)
Tuber native potato	Solution casting	Packaging	Montero et al. (2017)
Cereal corn Starch	Solution casting	Packaging	Montero et al. (2017)
Legume pea starch	Solution casting	Packaging	Montero et al. (2017)
Yam bean	Solution casting	Packaging	Asrofi et al. (2018b)
Yam bean	Solution casting	Packaging	Asrofi et al. (2018a)
Cassava bagasse Starch	Solution casting	Packaging	Teixeira et al. (2009)
Ramie starch	Solution casting	Packaging	Lu et al. (2006)
Potato	Solution casting	Packaging	Chen et al. (2012)
Cassava Starch	Solution casting	Packaging	Syafri et al. (2018)
Bengkuang Starch	Solution casting	Packaging	Syafri et al. (2019)

application. Table 8.8 shows the comparison of mechanical properties of some of the milk protein films formed with plasticizer.

5.2 Advantages and Disadvantages of Protein Biopolymer

There are several advantages of protein biopolymer, especially for food packaging application such as highly nutritional quality, good potential to adequately protect food product from their surrounding environment and excellent sensory properties (Gupta and Nayak, 2015). Proteins also act as a flavor and carrier of antioxidant, besides improving the quality of food and bacteriostats. The proteins such as milk proteins (whey proteins and casein) (Su et al., 2010), gluten (Zhong and Yuan, 2013), corn (Aydt et al., 1991), peanut (Aydt et al., 1991), sunflower seed (Martinez et al., 2005), whey protein (Jooyandeh, 2011), soy bean (Zhang et al., 2010), gelatin from collagen (Gómez-Guillén et al., 2011), soy protein (Tian et al., 2011), and wheat (Aydt et al., 1991) are suitable for the fabrication of protein biopolymer film due to its nutritional properties.

This type of biopolymer is also being used in nonedible packaging. Protein-based biopolymer also had impressed gas barrier properties compared with those prepared from polysaccharides and lipids (Cuq et al., 1998). Amazingly, the oxygen gas (O_2) permeability of the soy protein film was 670, 540, 500, and 260 times lower than that of pectin, starch, low density PE, and methyl cellulose, respectively, when they are not moist (Cuq et al., 1998). One of the disadvantage of soy protein film is low moisture barrier properties. This is because of their hydrophilic property and the considerable amount of hydrophilic plasticizer used in film preparation (Cuq et al., 1998).

TABLE 8.7
Some Research Using Different Protein Bases in the Preparation of Films Combining Strategies to Improve the Properties of Films.

Protein Type	Strategies	Effect Observed	References
VEGETABLE PROTEIN			
Amaranth	Native waxy and maize starch nanocrystals	Structure reinforcement	Condés et al. (2015)
Bitter vetch (*Vicia ervilia*) seed/ corn zein	Bilayer	Improved structure	Arabestani et al. (2016)
Canola		—	Shi and Dumont (2014)
Pea	Lysozyme	Antimicrobial	Fabra et al. (2014)
Sesame meal	—	—	Sharma and Singh (2016)
Soy	Chestnut (*Castanea mollissima)* bur extracts	Antioxidant	Wang et al. (2016)
Soy protein isolate	Peanut protein nanoparticles	Structure reinforcement	Li et al. (2015)
Soy/agar	Blend/extrusion	Structure reinforcement	Garrido et al. (2016)
Sunflower protein	Clove essential oil	Structure reinforcement and improved food shelf life	Salgado et al. (2013)
ANIMAL PROTEIN			
Argentine anchovy (*Engraulis anchoita*)	Sorbic or benzoic acids	Antimicrobial	Rocha et al. (2014)
Chicken feet	—	—	Lee et al. (2015a)
Fish gelatin	Chitosan nanoparticles	Structure reinforcement	Hosseini et al. (2015)
Gelatin	Longan seed extract	Antioxidant	Sai-Ut et al. (2015)
Porcine meat and bone meal	Coriander oil	Antimicrobial	Lee et al. (2015b)
Shrimp (*Litopenaeus vannamei*) muscle	Cinnamaldehyde/thermal treatment	Cross-linking	Gómez-Estaca et al. (2014)
Whey protein	Gum tragacanth	Structure reinforcement	Tonyali et al. (2018)
Whey protein	Ultraviolet treatment	Structure reinforcement	Díaz et al. (2017)
Whey protein isolate	*Lactobacillus rhamnosus*	Antimicrobial	Beristain-Bauza et al. (2016)
Whitemouth croaker muscle	Pink pepper phenolic	Browning reduction	Romani et al. (2018)

5.3 Application of Protein Biopolymer

Several scientists had conducted studied on the protein-based edible films such as corn zein films on nut and fruit products, whey protein film, casein emulsion film, and soy protein film for food packaging applications (Calva-Estrada et al., 2019; Gennadios, 2004; Rhim et al., 2004; Schmid and Müller, 2019). The polymeric characteristics of the protein film have been used for edible food packaging application (Khwaldia et al., 2010; Oussalah et al., 2004; Su et al., 2010; Zhang et al., 2010), but for nonfood packaging application, the major problems are an advancement of mechanical properties (such as tensile modulus, shear strength, flexural, elasticity, strength, and toughness). Table 8.9 displays packaging and biomedical applications of protein biopolymer. Besides that, biocompatible materials from proteins biomaterials have been utilized to develop scaffolds for various biomedical applications such as drug delivery, tissue engineering, wound dressings, and membrane filters. Fig. 8.5 shows the images of CMC (carboxymethyl cellulose)/SPI (soy protein isolate) film. This film is made up by a continuous

TABLE 8.8
Mechanical Properties of the Milk Protein Film Formed in the Presence of Different Formulation of Plasticizers.

Film	Tensile Strength (MPa)	Elongation at Break (%)	References
Sodium caseinate/ glycerol (4: 1)	10.5	17.4–26.7	Siew et al. (1999)
Sodium caseinate/ glycerol (2: 1)	73.7 –84.2	10.9–11.7	
Sodium caseinate/ PEG (4.54: 1)	5.3	10.9–16.35	
Sodium caseinate/ PEG (1.9:1)	25.4	10.9–13.9	
Whey protein/ glycerol (5.7/1)	4.1	29.1	McHugh et al. (1994) and McHugh and Krochta (1994)
Whey protein/ glycerol (2.3/1)	30.8	13.9	
Whey protein/ sorbitol (2.3/1)	1.6	14.0	
Whey protein/ sorbitol (1/ 1)	8.7	14.7	

TABLE 8.9
Packaging and Biomedical Applications Made From Protein Biopolymer.

Protein Biopolymer	References
PACKAGING APPLICATION	
Gluten films	Hemsri et al. (2011), Zhong and Yuan (2013), Zuo et al. (2009)
Milk protein films	Banerjee et al. (1996), Chen (1995), Kinsella and Morr (1984), Su et al. (2010), Vachon et al. (2000), Yoo and Krochta (2011)
Soy protein films	Park et al. (2000), Rangavajhyala et al. (1997), Rhim et al. (2006), Stuchell and Krochta (1994), Su et al. (2010), Tian et al. (2011), Zhang et al. (2010)
Corn zein films	Khwaldia et al. (2010), Lim and Jane (1994), Pol et al. (2002)
Gelatin films	Avena-Bustillos et al. (2011), Carvalho and Grosso (2006), Sobral et al. (2001)
Silk protein films	Jiang et al. (2007), Zhang et al. (2004)
BIOMEDICAL APPLICATION	
Scaffold in tissue engineering	Haghpanah et al. (2009), Hu et al. (2010)
Drug delivery systems	Cho et al. (2008), Koutsopoulos et al. (2009), Qiu and Park (2001), Torchilin (2005)
Biosynthetic hybrid hydrogels scaffold	Almany and Seliktar (2005)

casting method. Remarkably, this film can be produced simply with absence of puncture and cracks. Besides that, the film produced has a good flexible and durability, as much as it is necessary to be rolled into forms for sensible applications (Su et al., 2010).

6 CHITIN AND CHITOSAN

6.1 Properties of Chitin and Chitosan

Chitin is a polysaccharide with linear chains comprising of 2-acetamide-2-deoxy-β-D-glucopyranose units, which are linked by glycosidic bonds β(1 → 4) (Ma et al., 2019). Chitin exists as the second most abundant organic substance in the biosphere, surpassed only by cellulose, but chitin surpasses the latter in terms of replacement rate, which is twice as high as cellulose (Deringer et al., 2016). Chitin is found in the skeletal structure of invertebrates, such as arthropods, annelids, mollusks, and coelenterates, and in the cell walls of

FIG. 8.5 Photographs of CMC/SPI film in expanded and rolled states fabricated by a continuous casting method (Su et al., 2010).

diatoms and some fungi (Nataraj et al., 2018). Depending on the organism, chitin adopts different polymorphic structures called α-, β- and γ-chitin. The different polymorphic structures of chitin correspond to different arrangements in solid state (Pighinelli, 2019). The α-chitin is found in rigid and resistant structures, such as the arthropod cuticle. This chitin is usually associated with proteins, inorganic materials, or both (Deringer et al., 2016). The β- and γ-chitin occur in flexible structures and are also resistant. The α-chitin is the most abundant form and is considered the most stable, considering that the conversion of β- and γ-chitin in the first one is irreversible (Deringer et al., 2016).

Chitosan is commonly made by alkaline deacetylation of α-chitin. Chitin and chitosan are important linear polysaccharides consisting, respectively, of 2-acetamide-2-deoxy-β-D−glucopyranose (GlcNAc) and 2-amino-2-deoxy-β-D-glucopyranose (GlcN) linked by β(1 → 4) (Nataraj et al., 2018). Fig. 8.6 shows the molecular structures of chitin and chitosan. Chitosan solubilization can be attributed to protonation of the $-NH_2$ in the C−2 of D-glucosamine units in acid medium, which results in the conversion into a polyelectrolyte (Roy et al., 2017). The polycationic character of chitosan in acid medium is due to its weak base characteristic, thus its amino groups are easily protonated (Nataraj et al., 2018). Moreover, the hydroxyl groups of carbons 3 and 6 can also be protonated, which increases chitosan reactivity (Nataraj et al., 2018).

6.2 Advantages and Disadvantages of Chitin and Chitosan

Chitin is also fascinating in cosmetology because it is tolerable by the skin. It acts as an effective hydrating agent and a film-forming tensor having two benefits that are often cited: it provides water and it minimizes dehydration. The molecular weight of most chitosan-based products is too high that they cannot penetrate the skin, which is a crucial characteristic of a skincare product. These materials consist of chitosan hydrochloride, chitosan acetate, chitosan lactate, carboxymethyl chitosan, quaternized derivatives, oligosaccharides, and chitin sulfate and carboxymethyl chitin (Pighinelli, 2019).

Chitosan films have revealed remarkable results, possessing good mechanical properties and having the

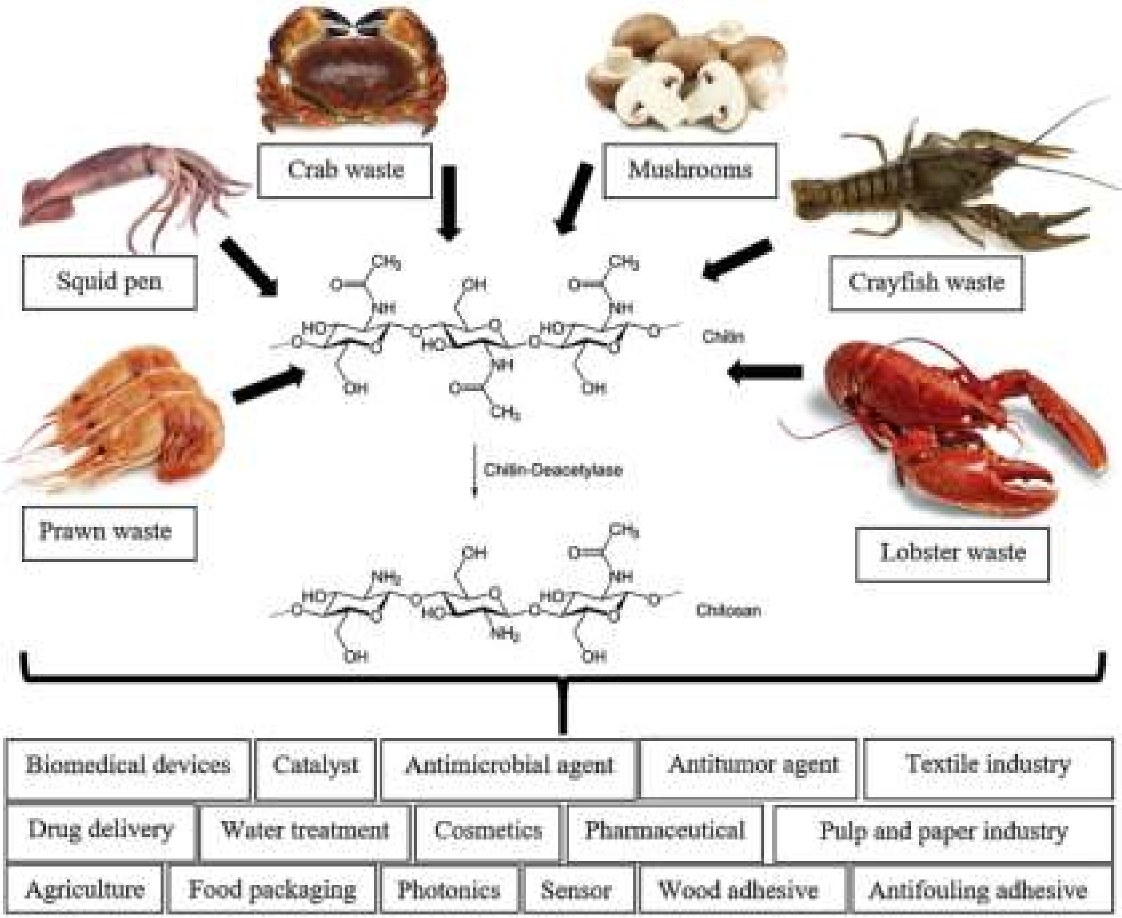

FIG. 8.6 Molecular structures of chitin and chitosan, their sources and applications.

advantage of the ability to integrate functional substances, for instance, as vitamins and carriers that release antimicrobial agents. Chitosan derivatives are advantageous due to the biocompatibility and safe, nontoxic to living tissues and their hydrophilic property, biodegradability, antibacterial activity, bioadhesivity, mucoadhesivity, and complexing property (Llanos and Tadini, 2018).

Chitosan has the ability to form gels in addition to having viscosity-related properties, complete biodegradability, and even antitumor influence, like alginate polysaccharide. Chitosan creates films permeable to air that aid cellular regeneration while protecting tissues from microbial attacks. Chitosan also stimulates the process of regeneration of tissues, making it a suitable material in artificial skin manufacturing for the applications in skin grafts on high degree burns and in surgical applications (suture threads) (Oryan and Sahvieh, 2017). In terms of health benefit, chitosan is able to trap lipids at its insolubilization pH along the digestive tract, which significantly reduces cholesterol level in the blood. Chitosan possesses bioadhesive properties that make it of interest in adhesive-sustained release formulation required. Mucoadhesivity permits to enhance the adsorption of drugs especially at neutral pH.

This natural polymer owns several inherent features making it an effective material for environmental purposes: (i) lower cost in comparison with activated carbon or organic resins available in market, (ii) outstanding pollutant-adhering capacities and outstanding selectivity, (iii) versatility, and (iv) biodegradability. Indeed, major applications of chitosan are based on its excellent capability to tightly bind a whole range of pollutants (Vidal and Moraes, 2019).

Researchers had summarized that the biosorbents are effective in pollutant elimination with the extra advantage of being cheap, nontoxic, and biocompatible.

Chitosan has gained substantial attention for developing microcapsules, which is advantageous as drug carriers due to their controlled release properties and biocompatibility (Rokhade et al., 2007). Presence of microcapsules also makes chitosan applicable for wall materials for textile finishing product encapsulation (Alonso et al., 2010). Numerous techniques have been used in the creation of chitosan microcapsules, such as spray drying and phase coacervation (Liu et al., 2011); the microcapsules yield is either single or multilayer, depending on microencapsulation method (Pothakamury and Barbosa-Cánovas, 1995).

Chitin and chitosan poses high organic solvent resistance, which is useful for separation membranes. This biomaterial is used with organic solvents, where chemical resistance is typical. Explicitly, chitin is highly acid resistant, meanwhile chitosan is highly alkaline resistant. These features contribute to the application of chitin and chitosan as separation membranes for a range of uses in response to specific requirements (Chaudhary et al., 2015).

However, chitosan films are unsuitable for packaging application due to the fact that they are highly permeable to water vapor. In addition, their hydrophilic character also make them to exhibit resistance to fat diffusion and selective gas permeability (Morin-Crini et al., 2019).

6.3 Application of Chitin and Chitosan

Chitin- or chitosan-based biomaterials are promising candidates to be used for wound healing, tissue engineering, and drug delivery. The fact that they are originated from the freely available natural sources has made them more economically stable compared with synthetic polymer materials. Moreover, their utilizations in biomedical field, such as scaffolds for tissue engineering, manages to minimize cost and manpower needed for second surgery to remove them, since chitin/chitosan-based materials are biodegradable. Besides, their biocompatibility also avoids the necessity for any treatments to be performed due to the rejection of implants fabricated from employing these materials. Currently existing chitin- and chitosan-based commercial products are as summarized in Table 8.10. The markets for chitin and chitosan are the United States, China, Norway, France, Poland, Japan, Germany, Korea, Canada, Australia, and the United Kingdom (Crini and Lichtfouse, 2016; Morin-Crini et al., 2019). In 2015, Japan has dominated (advanced in technology, commercialization, and utilization of these

TABLE 8.10
Commercial Products From Chitin and Chitosan and Their Applications.

Product	Manufacturer	Application	Patent/References
LipoSan Ultra	Primex	Weight loss	US 6130321, Johnson and Nichols (2000)
Slim MED	KitoZyme	Weight management and treatment	US 20040126444 A1, D'huart and Dallas (2004)
ChitoDot	Tricol biomedical, Inc.	Wound dressing and bleeding control	US 8269058 B2, McCarthy et al. (2012)
BST-Gel	Piramal Healthcare (Canada) Inc.	Chronic wound healing, bone filling, cartilage repair, invertebral disc regeneration	US 8747899, Chaput and Chenite (2014)
ChitoFlex PRO	Tricol biomedical, Inc.	Wound dressing and bleeding control	US 8668924 B2, McCarthy et al. (2014)
HemCon ChitoGauze PRO	Tricol Biomedical, Inc.	Wound dressing material	US 9205170 B2, Lucchesi and Xie (2015)
Talymed	Marine Polymer Technologies	Wound dressing material	US 9139664 B2, Finkielsztein and Vournakis (2015)
Protasan	NovaMatrix	Pharmaceutical application	WO 2015081304 A1, Francis et al. (2015)
Reaxon	Medovent	Nerve rejuvenation	

biopolymers) the industry market of chitin and chitosan accounting for 35%, which is equivalent to 700–800 tons per annual (Morin-Crini et al., 2019).

7 POLY(BUTYLENE SUCCINATE)

7.1 Properties of PBS

The world community is anticipated to grow to 9 billion by 2050, hence resulting in the increment of the plastic production and undoubtedly, plastic wastes (Emadian et al., 2017). These motivated researchers to explore and introduce bioplastics, such as PCL, polylactide (PLA), PBS, and TPS. PBS is identified as the most notable biopolymer that is produced via polycondensation of butanediol and succinic acid having unique features, such as good melt processability, great toughness, high chemical resistance, high heat distortion temperature, biodegradable, good mechanical properties, high chemical, and thermal resistance (Boonprasith et al., 2013). This biopolymer is derived from natural sources (Jamaluddin et al., 2016). PBS is a thermoplastic polymer resin in the polyester family. PBS comprises of polymerized units of butylene succinate with repeating $C_8H_{12}O_4$ units. There are two ways to synthesize PBS:

1. Transesterification process (from succinate diesters)
2. Direct esterification process (from the diacid).

The typical route in PBS production is direct esterification of succinic acid with 1,4-butanediol, which involves two steps. First, excess of diol is esterified with diacid to from PBS oligomers with water as by-product of process. Next, these PBS oligomers are trans-esterified under vacuum condition with the presence of catalyst (zirconium, germanium, titanium, or tin) in order to produce a high molecular weight (Mw) polymer that is PBS as shown in Fig. 8.7.

The physical properties of poly(butylene succinate-co-butylene adipate) copolyesters can vary with comonomer content, as tabulated in Table 8.11 and Fig. 8.8.

7.2 Advantages and Disadvantages of PBS

PBS are synthesized using succinic acid. Succinic acid is also obtainable from the fermentation of microorganisms on renewable feedstocks, for instance, glucose, starch, xylose, etc (Song and Lee, 2006). *Actinobacillus succinogenes*, *Anaerobiospirillum succiniciproducens*, *Mannheimia succiniciproducens*, and recombinant *Escherichia coli* are well-known and well-established bacterial production strains that can produce succinic acid (Gigli et al., 2016; Song and Lee, 2006; Xu and Guo, 2010).

Biodegradability is another useful characteristic of PBS biopolymer, since the need of surgery to remove the carrier/implant can be prevented as it self-degrades when its desired function has ended. It is worth stating that not only the biomaterial but also the degradation products are nonhazardous for the host.

Conversely, PBS has attention-grabbing physiomechanical properties and can be simply synthesized by melt polycondensation at reasonable costs. Added value is given by the ability to achieve both succinic acid and 1,4-butanediol from renewable resources, which marks PBS a completely bio-based and biodegradable polymer.

7.3 Application of PBS

As PBS disintegrates naturally into water and CO_2, it offers as a biodegradable substitute to some commonly used plastics. The range of PBS application areas is still expanding and several areas can be recognized, but it remains hard to know explicitly in which specific object PBS is really used. In packaging field, PBS is converted into films, bags, or boxes, for both food and cosmetic packaging. PBS also could be found in disposable merchandises, such as tableware or medical articles. Next, in agriculture, PBS is useful in the manufacturing of mulching films or delayed release materials for pesticide and fertilizer. PBS is also promising to find market shares in fishery (for fishing nets), forestry, civil

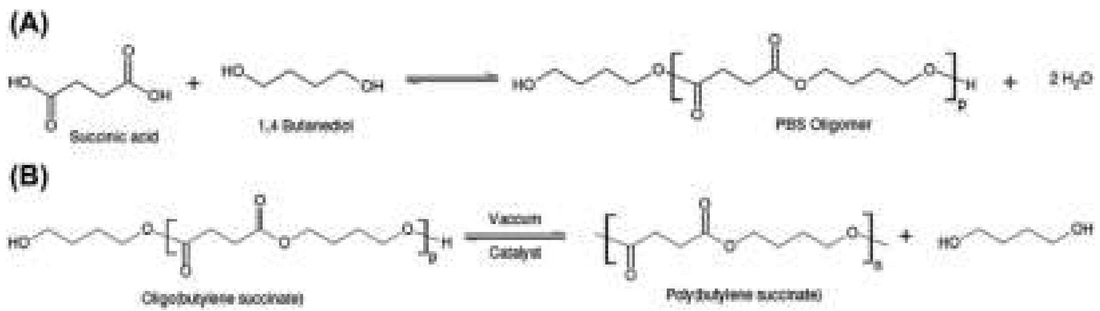

FIG. 8.7 PBS synthetization process using direct esterification process: **(A)** first step and **(B)** second step (Jamaluddin et al., 2016).

TABLE 8.11
Thermal Properties and Degree of Crystallinity of PBSA Random Polyesters (Xu and Guo, 2010).

Polymer	ΔH_m (J/g)	ΔH_m{{\tf="PSMPi4"\char56}} (J/g)	T_m (°C)	T_g (°C)[a]	Crystallinity[b] (%)	Crystallinity[c] (%)
PBS	67.4	110.3	112	−18	61.1	39.66
PBSA-5[d]	96.0	110.3	108	−21	87.0	54.47
PBSA-10	72.5	110.3	103	−23	65.7	45.83
PBSA-15	79.8	110.3	99	−27	72.3	45.27
PBSA-20	59.5	110.3	92	−34	53.9	46.83

[a] The glass transition temperature (T_g) was adopted from the tanδ peak measured by dynamic thermal analysis.
[b] The degree of crystallinity was the ratio of melting enthalpy determined by DSC to the melting enthalpy of completely crystalline PBS (100 J/g).
[c] The degree of crystalline was calculated from WAXD results.
[d] The number indicates the molar percentage of adipic acid in the total feed acids for synthesis of PBSA copolyester.

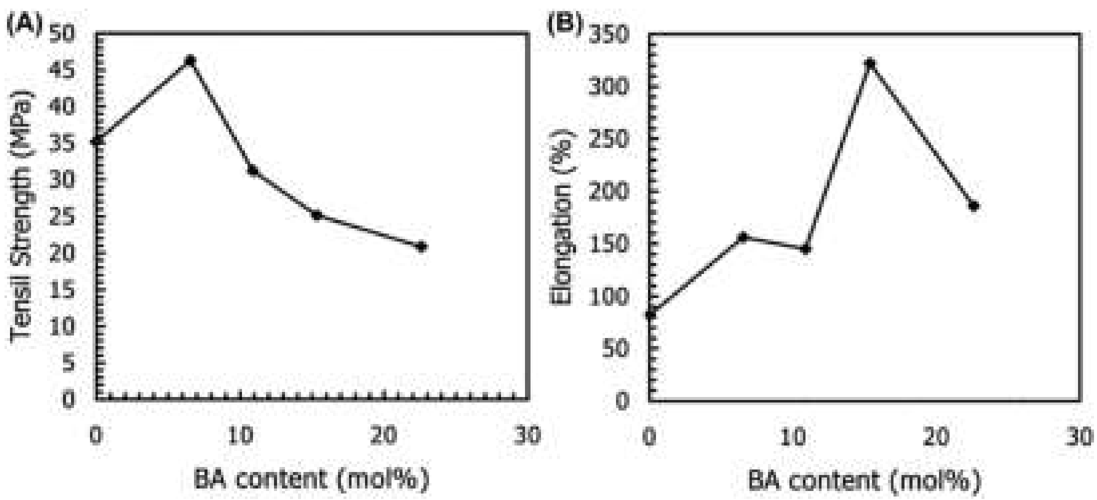

FIG. 8.8 The mechanical properties of PBSA at different contents of butylene adipate (BA) content: **(A)** Tensile strength and **(B)** Elongation at break (Xu and Guo, 2010).

engineering, or other fields in which recovery and recycling of materials after utilization is challenging. In medical field, PBS is adopted as biodegradable drug encapsulation system and is also being studied for implants.

8 SUMMARY AND FUTURE PERSPECTIVES

The progress of bio-based polymers as substitution for petroleum-based synthetics has been an area of attention due to the nondegradable and nonrenewable nature of synthetic plastics, as well as a primary research challenge for scientists. With the future fossil fuel crisis, the exploration and expansion of alternative chemical/material alternatives is crucial in minimizing mankind's reliance on fossil fuel resources. Some of the probable substitute candidates are PHA, PLA, starch, protein, chitin, chitosan, and PBS. Bio-based polymers are generally defined as polymers manufactured from renewable resources, comprising of three different categories: (1) natural polymers originated from biomass such as the agropolymers from agroresources, e.g., starch, cellulose, protein, chitin, and chitosan; (2) polymers formed by microorganisms, e.g., PHA; and (3) synthetic biopolymers, which are chemically synthesized using monomers obtained from agroresources, e.g., poly(lactic acid) and PBS, which is biodegradable as well. Overall, bio-based polymers are still new, though, they are in continuous development. Research attempts are obviously intent on addressing challenges constraining the use of bio-based polymers, comprising reduction the production and processing costs, improving barrier and mechanical properties, or introducing extra functions as active and smart packaging. Being a carbon neutral and valuable polymer manufactured from many renewable carbon sources by microorganisms, PHA is said to be a sustainable and environmental-friendly material. However, nowadays, PHA is not cost competitive compared with fossil-derived products. PLA is also produced from renewable sources having high tensile strength and modulus and can be processed via conventional processing methods. Starch complies all the principle aspects; hence, it is suitable for edible coatings/films. Chitin is the most abundant natural amino polysaccharide and is predicted to be produced yearly almost as much as cellulose. It has grabbed great attention not only as an underutilized resource but also as a new useful material of great potential in many fields, and current progress in chitin chemistry is quite remarkable. PBS is a renowned aliphatic polyester, provided its fascinating thermomechanical properties and the proven biodegradability, combined with acceptable raw material and production costs. As a conclusion, biodegradable plastics are often reflected as savior products. Shifting to these materials would lessen carbon dioxide, greenhouse gas emission levels, energy of manufacturing, and amount of waste produced and create opportunity for new plastic industries.

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