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Review

Applications of Starch Biopolymers for a Sustainable Modern Agriculture

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Citation: Gamage, A.; Liyanapathiranage, A.; Manamperi, A.; Gunathilake, C.; Mani, S.; Merah, O.; Madhujith, T. Applications of Starch Biopolymers for a Sustainable Modern Agriculture. *Sustainability* **2022**, *14*, 6085. https://doi.org/10.3390/su14106085

Academic Editor: Shashi Kant Bhatia

Received: 1 April 2022
Accepted: 14 May 2022
Published: 17 May 2022

Abstract: Protected cultivation in modern agriculture relies extensively on plastic-originated mulch films, nets, packaging, piping, silage, and various applications. Polyolefins synthesized from petrochemical routes are vastly consumed in plasticulture, wherein PP and PE are the dominant commodity plastics. Imposing substantial impacts on our geosphere and humankind, plastics in soil threaten food security, health, and the environment. Mismanaged plastics are not biodegradable under natural conditions and generate problematic emerging pollutants such as nano-micro plastics. Post-consumed petrochemical plastics from agriculture face many challenges in recycling and reusing due to soil contamination in fulfilling the zero waste hierarchy. Hence, biodegradable polymers from renewable sources for agricultural applications are pragmatic as mitigation. Starch is one of the most abundant biodegradable biopolymers from renewable sources; it also contains tunable thermoplastic properties suitable for diverse applications in agriculture. Functional performances of starch such as physicomechanical, barrier, and surface chemistry may be altered for extended agricultural applications. Furthermore, starch can be a multidimensional additive for plasticulture that can function as a filler, a metaphase component in blends/composites, a plasticizer, an efficient carrier for active delivery of biocides, etc. A substantial fraction of food and agricultural wastes and surpluses of starch sources are underutilized, without harnessing useful resources for agriscience. Hence, this review proposes reliable solutions from starch toward timely implementation of sustainable practices, circular economy, waste remediation, and green chemistry for plasticulture in agriscience

Keywords: biodegradable polymers; starch; mulch films; composites

1. Introduction

Rapid industrialization, expansions in the global economy, and exponential population growth have caused extreme consumption of plastics and plastic-related products in our everyday life. Low cost, lightweight, ease of processing, and durability have led to widespread use of fossil-based petrochemical plastics in every sector, including food and agriculture [1]. Plasticulture in agriscience use 12.5 million tons of plastic products [2].

Polyolefins are widely consumed commodity plastics comprised of various subcategories such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polycarbonate (PC), polystyrene (PS), and others. PE and PP are predominant in agricultural activities and are named "plasticulture," mainly existing in mulch, low tunnels, greenhouse covers, solarization film, fumigation film, and packaging [3]. Plasticulture has spread across the world within a short period [4–6] as the demand continues to rise. Therefore, the use of plastic films has drastically increased every year, with global market demand valued at 3.9 million MT annually, for which Asia contributes (~70%) and Europe (16%) [7,8]. The most significant global greenhouse cluster spread across the Far East (China, Japan, and Korea) and is responsible for 8% of the global share, while 15% is produced in the Mediterranean area. Plastic film usage for agricultural applications in the Middle East and Africa has been increasing by 15–20% per year. With a 30% progressive annual growth rate, China is the largest consumer of plastic films and has reported consuming one million MT volume of plastics per year in agriculture, mainly for mulching 18,000,000 ha, low tunnels 920,000 ha, and greenhouses 1,300,000 ha. Plastic materials are a pivotal necessity in modern agriculture and play an important role [9,10]. Applications of plastics in agriculture are mainly related to crop production and micro-irrigation, forestry, livestock production, and aquaculture and fishery, as given in Figure 1.

Crop production and irrigation	Livestock production	Aquaculture and fisheries	Forestry
Greenhouses	Bale nets	Fishing nets	Tree labels
Low Tunnels	Silage tubes	Ropes and strings	support ties
Mulching films	Nets	Iceboxes	Fuel containers
Shade and protection nets	Trays	Floats	Tree guards
Nursery pots/seedling trays	Barn covers		
Reusable containers/crates	Ear tags		
Polymer-coated fertilizer	Ropes and twines		
Budding/grafting/supportive tapes and clips	Feeding containers		
Pesticides containers and sprayers			
Storage bags/crates			
Irrigation pipes			
Drip irrigation tubes			
Drainage pipes			
Tanks for liquid storage			

Figure 1. Applications of plastics in agriculture (photos courtesy of Priyantha Kumara, Sri Lanka; Nathasha Kodikara, Clyde North Victoria, Australia, and Thevin Randika, Sri Lanka).

Synthetic polymers from petrochemical routes and other sources of natural gas led to the depletion of non-renewable resources of fossil fuels that are finite in quantity and require millions of years to generate. Fossil fuel-based synthetic polymers exhibit low susceptibility to degradation under natural conditions and are considered non-biodegradable. A large fraction of agricultural plastics is mismanaged in landfills and accumulates on the Earth's surface, creating large dump yards. These plastic wastes take billions of years to degrade naturally. Plastic degradation is a gradual process that involves the breaking of molecular bonds containing hydrogen, carbon, and a few other elements such as nitrogen and chlorine. Therefore, the rapid accumulation of plastics on the Earth's surface may lead to massive environmental issues. End products of plastic degradation have extended retention in our geosphere. Furthermore, they tend to spread across the oceans, causing irreversible disastrous impacts on our ecosystems. Using plastics in high volumes such as polystyrene, polyethylene, and polypropylene poses substantial environmental challenges in safe recycling, reusing, and disposal. Incineration of onsite landfills has become common in agricultural solid waste management, associated with potential adverse exposure to heat and volatile toxic emissions such as ammonia, sulfur dioxide, organic corrosives, dioxins, etc. Ash generated from the combustion of agricultural plastic wastes may change the composition and pH of the soil, creating unfavorable conditions for cultivation. Strategies that have been introduced to manage polymeric wastes in modern contexts face challenges in execution due to toxic emissions from incineration, expensive separation processes for the recycling process, and presumable contaminations. Such drawbacks would reduce the process sustainability in reusing, recycling, incineration, and the energy recovery system [11].

Starch is a promising polysaccharide from abundantly available renewable sources and can be formulated either as a replacement raw material for fossil fuel-based plastics or as an additive in agriculture. Unique environmental safety measures of starch can be described in terms of absorbency, biodegradability, biocompatibility, and non-toxicity. Thereby, applications of starch are not limited to agriculture but are also significant in the food and biomedical industries [12–15]. Moreover, they are widespread in food, textile, chemical, pharmaceutical, and paper manufacturing. There is growing demand for starch in other industrial applications in packaging additives, adhesives, non-food fillers, and textile stiffening agents [16].

Starches can be extracted from edible plant sources such as potato (*Solanum tuberosum*), cassava (*Manihot esculenta*), corn (*Zea mays*), rice (*Oryza sativa*), wheat (*Triticum aestivum*), barley (*Hordeum vulgare*), etc. Starch is a staple food in some parts of the world, playing a vital role as an efficient source of carbohydrates and hunger management. Starch extraction from food sources can be problematic as it may reduce starch availability and aggregate hunger issues. Therefore, engineering starches from other non-edible sources for industrial purposes is a commercially viable replacement for bioplastics. Wild species of socoyam (*Caladium bicolor*), sweet yam (*Dioscorea villlosa*), false yam (*Icacina trichantha*), and oyster mushroom (*Pleurotus ostreatus*) are well known non-edible sources to extract starches [17]. Starch is a semicrystalline homopolymer organized as a high degree of supramolecular granules up to 20–40% crystallinity [6,18]. There are two major constituents in starch, amylose and amylopectin. Amylose has a liner polysaccharide structure and contributes up to 15–35% of the granules content in most plants. Some amylose molecules, particularly those of large molecular weights, may be constructed with ten or more branches. Amylopectin has the alpha-glucose units in its polymeric structure that are interlinked linearly with α (1→4) glycosidic and α (1→6) (5%) bonds, repeating at intervals of 24 to 30 glucose subunits, as explained in Figures 2 and 3. The main crystalline domains of starch granules are formed by amylopectin. Branched entities of amylopectin and amylose construct amorphous regions [7,19]. Structural co-crystallinity may occur due to amylose crystallization into a single helical structure [20]. Comparative abundance and variations in crystallinity, amylopectin ratio, moisture content, molecular mass, degree of branching, and polymeric chain length are dominant native characteristics of starch sources [18,21].

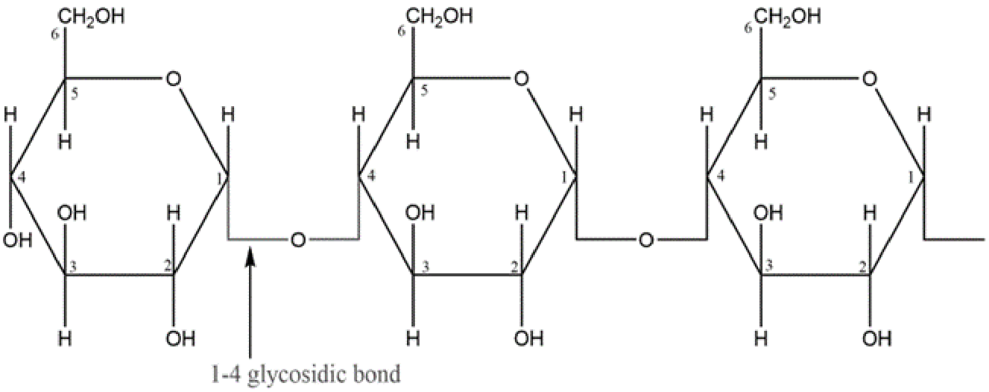

Figure 2. Structure of the amylose.

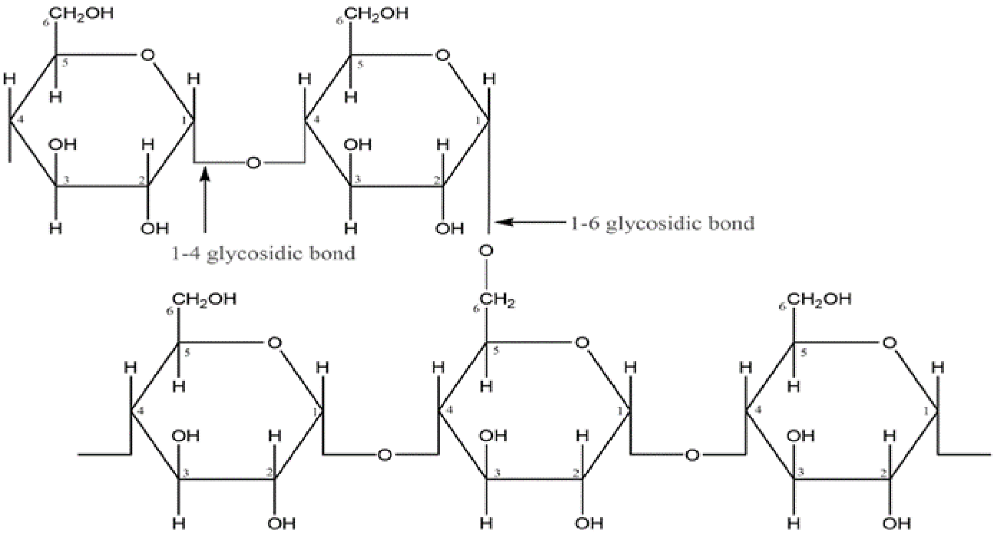

Figure 3. Structure of amylopectin.

Crystallinity is an inherent property of linearly organized structural domains of the starch polymeric matrix. The degree of crystallinity is a specific and unique property and plays a significant role in governing physio-mechanical, chemical, structural, degradation, processing, and storage properties of starch. The crystallinity of starch/composites has two descriptions [22–25]: (1) residual crystallinity is the inherent crystallinity that can be altered due to incomplete melting in starch processing; (2) processing-induced crystallinity occurs as a result of thermal processing with the presence of amylose and crystallinity extenders in formulations. In the gelatinization process, the crystalline structure of starch granules is altered and distorted. Furthermore, this process involves swelling in starch granules and melting of native crystalline domains followed by molecular solubilization [25–29].

The environmental properties of starch biopolymers can be described in terms of their physical properties, thermal properties, biodegradation, and environmental impact. Starch undergoes multiple physicochemical reactions during processing and its lifespan, such as water diffusion, granule expansion, gelatinization, decomposition, melting, and crystallization. The hydrophilicity and brittleness of starch films cause limitations as a replacement for plasticulture. Chemical modifications, surface functionalization, blends, and composites with other synthetic and biopolymers may turn starch into a viable alternative for petrochemical plastics. Starch and starch-based composites are a feasible techno-commercial strategy for agricultural films and other packaging materials due to their favorable low-cost factors, natural abundance, and inherent capacity to degrade readily in natural and aquatic environments [30,31]. This review discusses the current status of synthetic/biodegradable plastics in food and agroeconomic systems. Further, we aim to highlight the recent progress and challenges in utilizing starch and starch-based composites/blends of biodegradable polymers for agricultural applications. Table 1 contains information on various starch sources and differences in amylose, amylopectin, and crystallinity.

Table 1. Amylose, amylopectin, and crystallinity of starch from various sources.

Starch Source	Amylose (%)	Amylopectin (%)	Crystallinity (%)	References
Roots and tubers				
Potato	17–24	76–83	23–53	[32–37]
Cassava	16–22	81–83	31–59	[32,34,36–39]
Sweet potato	18	81		[34]
Yam	15–22	78–91		[37,38]
Cereals and pulses				
Corn	17–28	72–83	43–48	[32,34–37,40]
Rice	15–35	65–85	38	[32,34–37,41]
Wheat	20–25	75–80	36–39	[32,34–37,41]
Smooth pea	33–50	50–67	30	[34,42]
Wrinkled pea	61–88	12–39	17	[34]
Barely	27.5	72.5	37–44	[34,43]
Lentil	29–45	71–54	32	[34]
Sorghum	25	75	22–28	[36,44,45]

2. The State of Plastics Uses in Agriculture

2.1. Plastic Films in Agricultural Applications

In early 1950, the use of low-density polyethylene (LDPE) to replace vegetable paper mulching in agriculture was initiated and later gained significant popularity. Plastic films have revolutionized modern agricultural developments to convert barren lands to fertile lands (such as deserts). Hence, plastics carry paramount importance in all aspects of agricultural and horticultural processes [9,46–48]. A wide range of plastics is used in agriculture that has been defined based on requirements of cultivation, agronomic practices, regional climate demands, and geographical conditions. The estimated total amount of plastic films used in agricultural practices was nearly 6.96 million MT in the year 2017 worldwide [49]. Plastic films are used for crop cultivation, mulching, and constructing greenhouse tunnels (Figure 1). Accounting for more than 90% of usage, plastic films designated for cultivation are considered the largest group of plastics in agriculture. However, only specific plastic categories are used for some sectors in agriculture for irrigation, silage, nets, etc. The most populated plastic films for cultivations are made of polyethylene (PE) in agriculture [50].

2.1.1. Greenhouse Cover

Plastic films are extensively used as greenhouse covers to facilitate protected cultivation. A greenhouse can be defined as a technique for providing regulated environmental conditions for plant growth and crop production, built with structural stability and favorable materials [48]. In greenhouse covers, more than 80% of the world spread market utilizes simple monolayer to complex three-layer films as per the technological requirement and can be constructed from various polymers, namely LDPE, ethylene-vinyl acetate (EVA), and ethylene-butyl acrylate (EBA) copolymers. Some contexts refer to using other polymers such as plasticized polyvinyl chloride (PVC) in Japan and linear low-density polyethylene (LLDPE) in some parts of the world. Plastics used in greenhouse covers have been evolving since the 1950s. In modern-day agriculture, the lifetime of greenhouse plastic films varies between 6 and 45 months, and performance attributes may depend on the photo stabilizers used, the geographic location, pesticides used, etc. [51].

Characteristics related to film sizes are described in terms of the type and structural dimensions that would govern the durability of the films. Thereby, widths range from 6 to 14 m, and thickness gauges from 100 to 200 µm are proposed. Plastic films used for greenhouse covers often have an 80 to 220 mm thickness gauge and are up to 20 m wide [51]. Various film fabrications and production methods are used to embody the desired thermal, physicomechanical, and optical performances to cater to specific agroeconomic preferences for plant growth. The following examples can be given [52,53]: (a) For mono and multi-layer films, either extrusion or co-extrusion can be used to obtain films up to five layers. (b) The use of ad hoc formulations produces functionalized films. (c) Cover films function as anti-drip, anti-dust, anti-fog, etc., to support the crop growth. (d) Cover films would regulate UV radiation, either reflecting UV radiation or being partially transparent. (e) Colored films induce photomorphogenesis as plants or by selective reflectance of IR in solar radiation (cooling effect). (f) Functionalized films designed for specific agronomical performance support farming; UV-B induced secondary plant metabolites [54]. Further explanation can be found in Figure 4. Many greenhouse covers can lead to waste-disposal problems. Traditional petroleum-derived plastics, especially polyethylene, are not readily biodegradable. They are resistant to microbial degradation, and accumulate in the environment.

Figure 4. (**a**) Poly-tunnel greenhouse complex in Sri Lanka (photo courtesy of Priyantha Kumara). (**b**) Close-up image of a poly-tunnel greenhouse in Sri Lanka (photo courtesy of Priyantha Kumara).

2.1.2. Mulch

Mulching designed from various materials would provide soil coverage to prevent the hindrance caused by the growth of weed species and regulate soil temperature. Mulching also in traditional agricultural practices and biodegradable materials from natural sources was used before using plastic films. The following materials were used in conventional agriculture: straw, hay, dried leaves, tree bark, cardboard, gravel, several natural kinds of fibers (from coconut husks and hemp), and non-biohazardous organic wastes. Plastic mulch films have drawn wide attention due to their functionalities, versatility, and agroeconomic significance. Key functionalities of the mulch films can be highlighted as maintaining soil wetness, regulating the solar radiation, limiting the growth of weed species, and preventing soil erosion from surface runoffs. Plastic films are convenient for agricultural use as they are easy to lay on the soil and may require special machines, and thereby can cover tens of hectares within a short timeframe. Plastic films can be supplied according to the customers' preference (several lines of holes with different sizes). Farmers have been using almost exclusively black films, which can block solar radiation [55]. Photo-selective films and colored films (white, green, or yellow) have been introduced as a recent trend in mulching for specific agricultural practices (Figure 5).

Figure 5. A polyethylene-based plastic mulch film used for tomato cultivation in Sri Lanka (photo courtesy of Priyantha Kumara).

2.1.3. Low Tunnels

A low tunnel can be described as a temporary structure typically 60 cm to 90 cm high above the ground used to cover the width of a growing bed. The films that apply for low tunneling are in thickness gauge between 20 and 150 micron, and are usually thinner than high tunnels and films. Low tunnels have a considerably shorter lifespan (6–8 months) in agriculture. Plastic films designed for low tunneling have high clarity, transparency, and thermal insulating properties. The most frequently used polymers are ethylene-vinyl acetate (EVA) or copolymers of ethylene-butyl acrylate (EBA). The extent of the low tunneling market shows high stability over the last decade with an annual growth rate of 15%, except in China. In the other parts of the world, the market volume of small tunnels is estimated to be 170,000 tons of plastic per year [51] (Figure 6).

Figure 6. Polyethylene-based low tunnels used for cultivation in Clyde North, Victoria, Australia (photo courtesy of Nathasha Kodikara).

2.1.4. Silage

Silage is a type of fodder fed to cattle, sheep, and other such ruminants, made from green foliage crops. Storing silage in wrapped bales and later preserving it by fermentation is a widely popular technique across the globe [56]. There are two types of bale-wrapping technique systems in practice, individual and in-line. Each bale is wrapped into a completely sealed, stand-alone unit or silo in the individual system. Concerning the in-line system, bales are positioned in end-to-end alignment; then large-round bale circumferential surfaces are wrapped using polyethylene films. Silage grass piles together with pulp from sugar beets are used to also store and ferment the product after harvest. Covered silage piles help temporarily store sugar beets and provide protection against rain. Hence, plastic silages are consumed in significant volumes across northern Europe towards the south. In the southern Europe region, plastic films are often used in agriculture for making greenhouses, tunnels, and irrigation pipes. However, data on plastic film consumption, usage, and surfaces of silage coverage in the world are a research gap that needs to be fulfilled [50] (Figure 7a).

Figure 7. Silage films (**a**) and nets (**b**) in Clyde North, Victoria, Australia. (photos courtesy of Nathasha Kodikara).

2.1.5. Nets

According to Castellano et al. (2008), plastic nets are described as interconnected threads through weaving or knitting. These nets are geometric structures with regular pores and facilitate the passing through of fluids. Plastic nets in agriculture are comprehended for numerous agricultural applications. These applications protect orchards and ornamentals from hail, wind, snow, or intense rainfall. Furthermore, plastic nets are used for greenhouses as shading material, and nets are used to provide shading in mushroom beds, ginseng, cattle, etc. [57]. Nets moderately modify as the microenvironment around a crop changes. Nets in agriculture are used to provide protection against insects and birds for harvesting and post-harvest practices. Among the many polymers in use for manufacturing nets, HDPE has been extensively used for agricultural nets, along with polypropylene (PP) nets widely used to produce non-woven layers. In general, two main net categories are manufactured: (1) nets for agricultural use; (2) nets for nonagricultural purposes. The nonagricultural purposes are shadings for car parking, permeable coverings, fences, textiles, and anti-insect nets (Figure 7b).

2.2. Piping, Irrigation and Drainage, and Packaging

The other plastics used in agriculture include piping, irrigation, drainage, and packaging practices [58]. However, plastic use for piping in agriculture is considered beyond plastic films and is linked with agro-irrigation/industry piping systems that consume relatively less than plastic films. In contrast, plastic piping systems have extended service life compared to films in agriculture, and extended insights about piping in agriculture are still a research gap.

3. Biodegradable Polymers and Research Gaps

3.1. Classification of Biodegradable Polymers, Polysaccharides, and Starches

Biodegradable materials comprise partially or entirely materials synthesized, extracted, or derived from biomass such as plants, animals, microorganisms, biogenic residues, and wastes [35]. Biodegradable polymers can be segmented into two major groups based on their chemical and structural origin, biobased and synthetic (manufactured). Biobased biodegradable polymers can be derived from biobased sources, such as plants, animals, microorganisms, biogenic sources, etc. Biodegradable-synthetic polymers are synthesized from chemical routes and have advantages over natural polymers for their versatility, consistency, performance, and scalability in processing. Hence, synthetic polymers deliver a diverse range of mechanical properties, and degradation rates can be altered according to need with excellent biocompatibility and biodegradation [58]. The classification of biodegradable polymers is illustrated in Figure 8.

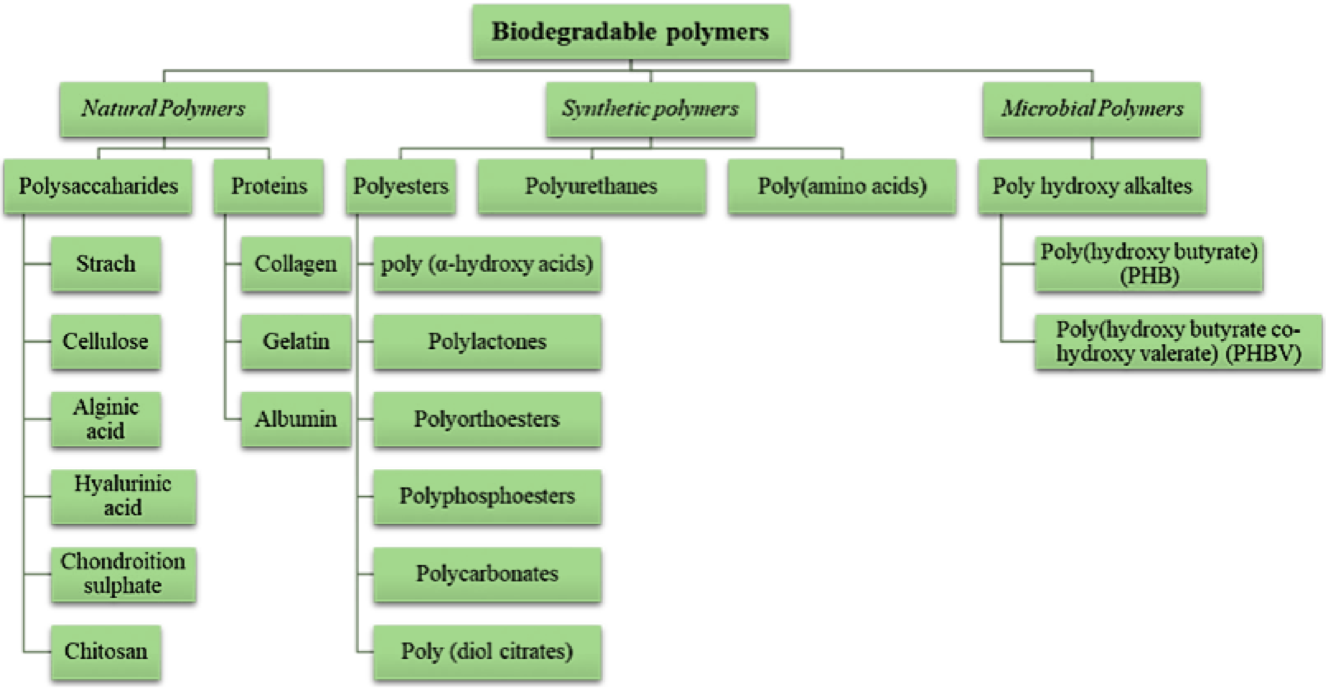

Figure 8. Classification of biodegradable polymers [59].

Cellulose and starch have been widely studied for their unique properties and performances in replacing highly consumed petrochemical polymers at a comparatively low cost [60,61]. Polysaccharides are the dominant group of biobased biopolymers and biomacromolecules. Starch and derivatives with different functional groups, chitosan, chitin, and cyclodextrin, have gained special attention due to their promising physiochemical properties, biodegradability, nontoxicity in nature, minimal efforts needed for extraction, abundancy, and the tendency for surface modification [62,63].

As per the classification in Figure 8, starch is the prominent natural polymer in the polysaccharide. Other than conventional starches from single-origin sources, nano-scale starch has captured vast attention in recent research due to its high surface-to-volume ratio, dense structure, biocompatibility, biodegradability, and high bonding strength [64]. Starch has been widely used in the plastic industry as a filler to produce eco-friendly and cost-effective plastic materials, blends, and composites. In the last ten years, starch has been used in plasticized form, thermoplastic starch (TPS), as the main component in polymer blends. Various plasticizers are used to prepare thermoplastic starch, such as glycerol, formamide, and urea [65]. Deriving starch-based sweeteners has been a well-known application concerning native and modified starches, namely glucose, fructose, and polyols such as sorbitol, mannitol, and maltitol. There are other food-related syrups, such as maltodextrins and oligosaccharides, that can be produced from starch. Derivative starches have been used as the thickening and gelling agents for several applications; such properties of native starches fail to meet process or product requirements [64].

Waxy starches are another subclass of starch that may not be directly relevant to agricultural applications, but used as a thickener and process aid for the food industry [66]. Due to the absence of amylose, waxy starches form weak viscoelastic gels containing high viscosity profiles, leading to suppressed retrogradation [67,68]. However, debranching waxy-starch chemistry has been given much importance in synthesizing nanoparticles and resistant starch [69–71]. Amylopectin starches have recently been discussed as a subsequent development of native starch processing. Amylopectin starch has a comparatively high amylopectin content as a result of leaching out amylose during processing [72,73]. Thereby, physicomechanical and structure properties of amylopectin starches may differ [74,75]. Kuzu and genetically modified potato species have been mentioned as sources of amylopectin starch [75–77].

3.2. Limitations, Research Gaps in Starch, and Surface Modifications

The main limitations of biodegradable polymers in agricultural applications include overall production cost, brittleness [78], and challenges in processing [79]. Thereby, blends of starch are a timely solution. Hydrophilic chemistry of starch makes incompatible, phase-separated, immiscible, and poorly dispersed blends and composites. To expand the scope of starch for agricultural applications, its inherent chemistry, such as hydrophobicity, paste clarity, thermal stability, retrogradation resistances, and physicomechanical process, must be altered [80]. Starch needs to be converted to make it viable for industrial applications as native starch has chemical and structural limitations. Addressing the poor mechanical, brittleness, and water insolubility of starch carries a vital commercial commodity product development that would expand starch applications for blends and plasticization [60]. Vacant hydroxyl chemistry in starch hetero-polymeric structure gives perfect reaction sites for surface modifications, physical, chemical, and enzymatic processing [81–84]. Furthermore, starch can be processed into hydrogels through mechanical, thermal, radical polymerization, complex crosslinking, etc. [85–88]. Surface modifications to starch would alter surface wettability or impart hydrophobicity or embody different functionalization. Due to process simplicity, associated low costs, scalability, and the absence of chemicals, physical methods have gained much acceptance in starch modifications. Such methods can be highlighted as osmotic pressure treatment, superheating of starch, instantaneous controlled pressure, iterated syneresis, Corona electrical discharges, thermally inhibited treatment (dry heating), pulsed electric fields treatment, micronization in vacuum ball mill, and mechanical activation—with stirring ball mill, drop (DIC) process [89–91].

On the other end, chemical modifications would advance the chemistry, the structure property, and the functionalization of starch. Chemical surface modifications such as oxidation, esterification, and etherification are successful approaches to hydrophobization of starch for active drug delivery and achieving homogeneous blends/composites [92,93]. Suspension co-polymerization, grafting onto, grafting from, and other polymer grafting methods are experimented with to embody different functionalizations concerning the starch matrix [94–97]. It is essential to execute modifications of starch by introducing hydroxyl, xanthate, carboxylate, acrylate, and amine phosphate groups [98]. Modern research has studied various modifications such as using plasticizers, crosslink formation, blending with other polymers, grafting, etherification, esterification, and dual modifications [98]. Crosslink formation and chemical substitutions are two common approaches applied for starch modification. Crosslink formation in the starch matrix improves stability concerning acid, heat, and shear, while introducing bulky substituents onto the starch matrix may reduce retrogradation. There are many non-food applications of starch in the paper, pharmaceutical (e.g., tablet formulations, encapsulating agents), cosmetics, chemical (e.g., adhesives, starch-based plastics), and textile industries. In order to meet requirements in non-food applications of starch, property alterations may be imparted from oxidation, cationization, copolymerization, hydrolysis, and substitution [99]. Cassava and potato tubers are considered comparatively favorable sources for isolating starch due to their tissue structure and low protein and fat content [100].

The botanical origin of the starch defines production processes, scalability, and associated costs. Remediations for improving properties may alter environmental safety and biodegradation of starch. This research describes the recent progress of starch blends in agriscience, different surface modifications, and degradation of starch blends/composites.

3.3. Starch Blending

Blends and composites are a strategy for cost reduction and property enhancements in biodegradable polymers. Blending two miscible phases in starch–polymer blends carries vital importance for dispersive and distributive mixing. Unfavorable surface chemistry of starch, such as surface wettability and hydrophilicity, may cause phase separation and poor distribution and also may lead to weak interfacial interactions in composites. This results in worsening the intended performance. Apart from the aforementioned surface modifications, developing efficient blending methods is crucial. Melt blending is a typical process in making starch-based composites, followed by injection molding, extrusion, blown film extrusion, laminations, etc. [101–103]. Solvent blending delivers a high degree of miscibility, filler distribution, and microencapsulation efficiency in starch films, which is ideal for blending hydrophobized starch [104–106]. In situ polymerization and grafting methods are mediated in advance blending [107,108]. Reaction extrusion has been described as promoting a higher degree of compatibility [109,110]. Further improvements and formulation efficiency of starch blends/composites can be achieved using compatibilizers, process aids, and plasticizers [56,111,112].

Starch is often blended with polymers and other matrices to improve the integrity in mechanical properties, thermal stability, and moisture absorption of starch [60,113,114]. Starch blending is defined as of paramount importance in reducing the production cost, improving barrier characteristics and dimensional stability, decreasing the hydrophilicity of starch, and increasing its biodegradability [60,113]. Starches are blended with low molecular weight plasticizers relevant to applications such as glucose, sorbitol glycerol, urea, and ethylene glycol [60,114,115]. The plasticizers are added to make starches softer and more flexible, decrease viscosity, increase their plasticity, or decrease friction. In thermoplastic starch (TPS) [113–116], between the plasticizer and the TPS matrix, the formation of hydrogen bonds occurs [117,118]. Depending on the type of plasticizer blended with starch, the final properties of TPS may vary. Plasticizers can enhance flexibility, extensibility, and fluidity by reducing strong intermolecular chain interactions. Moreover, TPS is a very hydrophilic material (Schwach and Avérous, 2004). Recent research highlights that starch blending TPS with biodegradable polymers plays a vital role in food packaging for various products [119].

3.3.1. Starch/PVA

Polyvinyl alcohol (PVA) is considered a biodegradable polymer from synthetic routes. PVA delivers excellent film-forming properties, a higher degree of conglutination, thermal stability, and gas barrier properties [115,120]. PVA blends may increase mechanical strength, water resistance, and weather resistance [121]. Gelatinization is a commonly used method for making starch and PVA blends, as the other techniques sound unfavorable due to the differences in thermo-degradation and the melting temperatures [121]. Loading more starch in PVA blends would reduce critical properties as a result of vigorous phase separation in blend preparation as the compatibility between PVA and starch enables it to form and exist as a continuous phase [119]. Many studies have been conducted using plasticizers, agents for crosslinks, fillers, and compatibilizers to improve the compatibility between PVA and starch phases [115]. Glycerol and water are some of the plasticizers used in promising blends [113]. In an aqueous glycerol medium, PVA and starch can be plasticized to form thermoplastic material [122]. Starch and PVA are proven biodegradable matrices under different biodegradation routes and environments. However, the degree of hydrolysis and molecular weight govern the biodegradability of PVA [119,123].

3.3.2. Starch/PLA

Polylactic acid (PLA) has been recognized as one of the most promising biodegradable polymers in recent research for biomedical, industrial, and packaging applications for its desirable biodegradable and hydrophobic properties. Commercial-grade PLAs are the copolymers of poly (L-lactic acid) and poly (D, L-lactic acid) [116,124,125]. Even though PLA has numerous advantageous properties, as mentioned previously, brittleness, ductility at service temperature, and low impact resistance limit PLA applications. Therefore, numerous plasticizers have been blended with PLA, such as poly(ethylene glycol), glucose monoesters, glycerol, citrate esters, and oligomers, to enhance the aforementioned properties. However, the starch/PLA blend offers superior qualities such as cost, properties, and biodegradability, which are the main objectives in industrial and process-related applications [116,124,125]. Starch is hydrophilic, while PLA is hydrophobic. Therefore, the blending of these two compounds may cause low miscibility. Compatibilizers such as amphiphilic chemicals or efficient coupling agents are added to achieve a higher degree of interfacial interactions and enhance miscibility between starch and PLA in melt blending and other processing techniques [114,126]. The compatibilizers in PLA blends are poly (hydroxy ester ether), PLA-graft-(maleic anhydride), PLA-graft-(acrylic acid), PLA-graft-starch poly (vinyl alcohol), and methylene diphenyl diisocyanate (MDI) [127].

3.3.3. Starch/PCL

Poly-ε-caprolactone (PCL) is a biodegradable linear synthetic polyester. This semi-crystalline polymer is well known as an aliphatic polyester synthesized by ring-opening polymerization of ε-caprolactone. Even though PCL is hydrophobic with a low melting point (at around 60–65 °C), radiation cross-linking treatment or blending it with other polymer melting points can cause improvement [128–130]. As the molecular weight and degree of crystallinity control the degradation rate of PCL homopolymers, the biodegradability of PCL can be extended from composites and blends of other aliphatic polyesters [128]. Moreover, in starch/PCL blends, with the presence of starch, the biodegradation of PCL is increased as starch intensifies hydrolysis reactions [131]. Blends of starch and PCL have been reported for undesirable phase separation because of incompatible hydrophilicity of starch and hydrophobicity of PCL [128]. Using interfacial coupling agents or compatibilizers is necessary to enhance the compatibility and miscibility of these two matrices. Recent studies have thoroughly assessed the interfacial chemistry of two interfacial agents, PCL-g-diethyl maleate (PCL-g-DEM) and PCL-g-glycidyl methacrylate (PCL-g-GMA), in a PCL–starch blend [132]; moreover, poly(ethylene glycol) (PEG) have been proven to improve PCL interfacial properties [128]. It has been a practice to incorporate PCL into starch to eliminate the weaknesses of pure thermoplastic starch. Starch lowers the degree of crystallinity; therefore, the enzymatic degradation is elevated by the crystallinity reduction of PCL [133,134]. Based on the studies that have been conducted on PCL–starch blends, PCL–starch blends may result in high production costs and inconsistent properties, which may limit applications [128].

3.3.4. Starch/PHB-HV

Among the many starch/PHB-HV studies, differential blend behaviors of polyhydroxybutyrate-hydroxyvalerate with corn starch at different concentrations have been evaluated [135]. Some blends show poor interfacial adhesion between starch and poly(hydroxybutyrate-co-hydroxyvalerate) (PHB-HV) also in heterogeneous starch granule dispersion over the PHB-HV matrix [135]. With adequate formulation and processing techniques, the aggregation between starch and PHB-HV can be reduced [136].

3.3.5. Starch/PBS and Starch/PBSA

Polybutylene succinate (PBS) is a commercially available thermoplastic polyester known for its low degree of crystallinity, which may lead to a low degradation rate. PBS has properties of great importance, such as excellent impact resistance, high thermal stability, and good chemical resistance [137]. The addition of starch to PBS as a filler improves the flexibility and accelerates the biodegradation time while expanding its applications in packaging and flushable hygiene products [136,138]. Co-polyester poly(butylene succinate-co-butylene adipate) (PBSA) has good mechanical properties, biodegradability, melt processability, and thermal and chemical resistance [139,140]. Aliphatic thermoplastic copolymers can be synthesized from polycondensation of 1,4-butanediol with succinic and aliphatic acids. The morphology and performances of melt-processed butyl-etherified starch and PBSA blends have revealed highly branched amylopectin embodied in starch to provide better chemical and interfacial interactions with the PBSA matrix compared to linear amylose structures [140].

3.3.6. Ternary Blends

Several studies have delivered solutions using ternary blends of PCL PLA and starch using acrylic acid grafted PLA70PCL30 as a compatibilizer in metaphase systems. The literature confirms that the addition of PCL to TPS/PLA blends may increase the ductility [141]. Substantial improvements in mechanical properties, impact resistance, and elongation at break in TPS/PLA blends could have been achieved by adding PCL [142]. Moreover, methylene diphenyl diisocyanate (MDI) is an efficient compatibilizer in ternary blends of TPS/PCL/PLA, enhancing tensile strength and elongation at break [143]. Other researchers have used poly(butylene adipate –co-terephthalate) (PBAT) to replace PCL, as PBAT is a co-polyester with higher chain flexibility and degradability [143]. Furthermore, some groups have evaluated the properties and performances of the ternary blends of TPS with the synthetic polymers PLA and PBAT. In those PBS blends, they maintained TBS 50% by weight. The remaining fraction was PLA and PBAT, which were added in various ratios using the compatibilizer anhydride functionalized polymer to integrate metaphases [144]. These compatibilized blends showed enhanced tensile strength, elongation at break, flexural strength, and flexural modulus compared to the non-compatibilized blends. As another study describes, PBAT has been used to elevate toughness in TPS/PLA blends [145]. Similarly, parallel research has assessed the loading effect of PLA and the respective functional properties of TPS/PBAT in blown films [146]. Incorporating PLA into the TPS/PBAT blends substantially impacted the opacity, viscoelasticity, and mechanical barrier characteristics of those blown films. Even though the films with PLA showed good water vapor barrier properties, due to their undesirable mechanical properties and thicknesses, they were considered unsuitable for flexible packaging. Furthermore, use of a suitable plasticizer to improve the processability of the aforementioned films has been suggested [146]. In recent years, many findings related to ternary blends of PHB, EVA, and starch have concluded that vinyl acetate content enhances the compatibility and homogeneity between PHB and EVA. Therefore, EVA can be considered one of the most critical modifiers for PHB/starch blends [147].

3.3.7. Nanocomposites: Fillers in the Starch Matrix

It has become one of the standard practices to make nanocomposites to reinforce starch. Nanofillers are extensively added to starch-based materials to enhance thermomechanical stability and biodegradability, and reduce hydrophilicity [148,149]. These nanocomposites can be prepared in combinations of inorganic or natural materials that inherit a charge of between 2% and 8% of nanoscale inclusions [150]. Nanofillers are of different types based on their shape, including spherical or polyhedral, single or multilayered, and nanosheets. These nanofillers provide a large superficial area while improving adhesion and matrix filler interactions between the polymeric matrix and fillers. The following research has reviewed various nanoscale fillers in polymeric matrices that have been plasticized using starch [151,152]: (a) phyllosilicates such as montmorillonite, hectorite, sepiolite; (b) polysaccharides such as cellulose, starch, chitin, and chitosan; (c) nanowhiskers/nanoparticles; (d) carbonaceous nanofillers, mainly carbon nanotubes, graphite oxide, carbon black, etc. Phyllosilicates are the most used nanofillers in starch blends and composites for enhancing properties due to unique filler characteristics such as natural abundance, low price, and high aspect ratio. Nano-fillers have excellent polymer interfacial interactions and would significantly improve mechanical and thermal properties resulting from large specific surface area and high surface energy [153]. Nanofillers such as chitin [154], and cellulose [155,156], nanocrystals such as chitin [154], nano-clay [157,158], nano-TiO_2, [153], and nano-$CaCO_3$ [148] have been used as efficient fillers for starch-based thermoplastics.

When considering the environmental friendliness, modified or synthesized-polysaccharide nanofillers may not sound ecologically competent as they undergo several pre- and post-chemical treatments in preparations such as acid hydrolysis [148].

3.3.8. Starch-Based Nanocrystals

Nanocrystals from starch-based sources are of great importance in their comparatively low production cost, renewability, and environmental friendliness. Nanocrystals from starch sources are engineered from chemical, physical, and mechanical processing, in which hydrolysis treatments are applied to the amorphous regions to release crystalline lamellae from native starch granules [159]. A positive reinforcing effect was obtained with the use of starch-based nanocrystals in reinforcing elastomer-based matrices while increasing both stresses at the break and relaxed storage modulus [160]. Incorporating starch-based nanocrystals in biocomposites delivers many advantages and enhancements, such as strength at break and glass transition temperature. However, additives have disadvantages, such as increasing water absorption and decomposition temperature [152]. Tang and Alavi have demonstrated that embodying starch nanocrystals in PVA nanocomposites and blends would enhance physical properties for industrial applications [113].

3.3.9. Essential Oils Impregnated Starch Blends

In order to improve mechanical, barrier, and antimicrobial characteristics, various essential oils were impregnated with starch composites/blends [161,162]. Essential oils are capable of improving the microstructure, morphology, and thermal processing of starch blends. Starch blends that have infused essential oils would facilitate active drug delivery for plant biocontrol and act as a biocide in organic horticulture [163,164]. Rosemary [165], oregano [166], cinnamon [165], and lavandin [167] are notable essential oils that have been successfully researched in metaphase starch blends. Infusion of essential oils may cause challenges; therefore, control processes such as microencapsulation and supercritical impregnation are in use [167,168]. The use of essential oils is most often combined with chitosan and titanium dioxide for achieving desired antifungal and antimicrobial properties in starch blends/composites [169–171].

3.4. Biodegradable Starch Polymers for Agriculture

3.4.1. Mulching

An innovative solution to the disposal of commercial plastic wastes could be the use of biodegradable plastic materials for agriculture. Biodegradation, or the breakdown of chemical structures throughout the action by microorganisms, is the critical process in transforming organic chemicals in the environment. Biodegradable films have been developed for agricultural purposes in the last decade, particularly mulching applications [172–177]. The plastic films based on natural renewable sources do not generate waste to dispose of, representing a sustainable ecological alternative for delivering environmentally friendly solutions. Thereby, biodegradable films make minimal impacts in our geosphere and can be integrated effectively into the soil as thermal, physical, and biosystems such as bacteria and enzymes convert them into respective degradation products, carbon dioxide or methane, biomass, and water [178]. In an alternative approach, biodegradable films can be blended with other organic components to formulate carbon-rich composts [178–182]. Many manufacturing methods are being used to make biodegradable films, such as extrusion (flat and blown film), injection molding, laminations, coating, etc. The literature highlights using thermo-plasticizing, spraying, and casting methods to form biodegradable films from biopolymers and polysaccharides such as starch for agricultural and packaging applications [183–187]. Furthermore, research has been conducted on cellulose [172], chitosan [188,189], alginate [176,190], and glucomannan [191] concerning employing new eco-friendly, sustainable materials for agricultural purposes.

Starch/chitosan-based biodegradable mulching for short-cycle crops, mainly for vegetables and flower crops, has been analyzed as a potential replacement aiming at fertilizer-free and microbial culture-based plant growth [192]. These starch/chitosan blends showed a two-fold decline in film solubility in comparison with the 100% starch films. Furthermore, these films exhibited a decrease in properties in the infrared spectrum and micrographs when in contact with the soil. However, there were no visible cracks in chitosan-starch films for 45 days, indicating the stability of the films and effective usefulness as biodegradable mulch [192]. There were indications that films that incorporated starch blends contain renewable content embodied for agricultural mulch [193]. These films are blends of starch/PVA/glycerol cross-linked films that were coated with a thin layer of PVC or any other plastic that showed good functional properties for agricultural mulch [193]. In a similar study, PLA and modified starch were blended with natural fibers to make fibrous composite films for mulch applications [194]. Biobased polyolefins continue to be the predominant category in mulching for agriculture as the market expands. Mulching makes a positive environmental impact by minimizing the requirement of pesticides, herbicides, water, and energy in agriculture. Most mulching films endure for a single growing season or multiple years, subjected to the crops and the agricultural practices employed [194].

3.4.2. Silage

Plastic films that are utilized to cover silage face many challenges in recycling due to extreme contamination by soil, sand, and other organic residues [195]. In comparison to other agricultural films, silage cover has a relatively short usage time (12 months). Moreover, these covers and bales have a high probability of improper disposal. Frequently, silage films ended up in landfills or burned in fields [195–197]. Biodegradable plastic film for silage covers can be derived from various routes from renewable biological sources or petroleum or a wide range of alternative petroleum-based sorts; among these, starch (potatoes and maize) and oleaginous plants (sunflower and rapeseed) are mainly discussed [198]. In the early 2000s, the biodegradable plastics derived from petro-chem sources were used to produce stretch films to wrap bales [199]. Eco-flex co-polyester introduced by BASF was the first prototype film that offered critical properties required to stretch films in silage bales, good mechanical properties, and sufficiently low oxygen permeability. In similar references, films stabilized by carbon black also fulfilled all these criteria. The aforementioned film types are often used to wrap silage bales to store bales beneath a roof or outside in a field. Silage bales are exposed and subjected to environmental attacks inside the bales and from contact surfaces between the soil and the film. Concerning co-polyester films that are used for silage bales, degradation should be substantially slower. Thereby, some research refers to improvements in extending degradation time by adding an adhesive layer limiting degradation or chemically modifying the film material to slow down the degradation rate [199]. In 2008, biodegradable new silage cover plastic films were developed from compostable resins based on renewable sources through research collaboration between the University of Turin (Italy) and Novamont SpA (Novara, Italy) [197]. These films were synthesized (early sample, model, or release of a product built to test a concept or process) using a starch-based polymer stand as Mater-Bi® (MB; Novamont SpA), which is established as the first completely biodegradable and compostable biopolymer invented [183].

3.4.3. Packaging and Containers

Packaging can be described as an element used to hold, protect, handle, deliver, and present goods involving raw materials to finished products, from producers to consumers. There are many ways packaging can be categorized, generally distinguished according to the primary raw material in packaging, and thereby it can be divided into metal, glass, polymer, paper, cardboard, wood, textile, monolayered, multilayered, ceramic, etc. [200]. Packaging functions as preservation, protection, merchandise, and a marketing and branding tool, and facilitates the distribution of goods. It plays a significant role in ensuring product safety (in handling, storage, transportation) and product quality, which are essential to consumers [201]. Food packaging defines an integral part of the preparation, production, preservation, storage, and distribution [200]. Required characteristics of food packaging are defined by the type of food products and shelf life. Green plants from various sources, such as potatoes, corn, wheat, and rice, are used for modern-day starch-based raw materials for biopolymers [200]. Thermoplastic starch, or TPS, represents the most widely used bioplastic category due to its pliable and moldable thermoplastic polymer characteristics at elevated temperatures, reshaping retention with solidification upon cooling. TPS has limited applications due to its relatively low water vapor and low mechanical properties. However, TPS achieves equilibrium properties after a few weeks [202]. Incorporating starch into aliphatic polyesters may enhance the performances required for packaging, mainly mechanical properties and biodegradation. A combination of starch with polyvinyl chloride (PVC) is used to produce completely biodegradable starch-based plastic films [203]. These starch films can be applied to diverse applications for bags, sacks, rigid packaging, hot-formed trays, and containers, and to fill gaps in packages. This category of material is a successful replacement for polystyrene and polyethylene in packaging because of their better strength [204]. Table 2 demonstrates critical packaging applications and other uses of starch-based biopolymers.

Table 2. Applications of starch-based polymer blends.

Blend	Properties	Applications	References
Starch/PVA	• Good film-forming • Strong conglutination • High thermal stability • Gas barrier properties	• Replacement of LDPE films in applications where barrier properties are not critical. • Water-soluble laundry bags • Biomedical and clinical field. • Replacement of polystyrene foams as loose-fill packaging material. • Packaging applications. • Starch forms are used for food packaging.	[113,205–207]
Starch/PLA	• Biodegradable and hydrophobic properties • With 30 wt% of modified Starch/PLA blends demonstrated higher tensile strength and ductility than PLA blends with unmodified starch	• Food packaging, electronic devices, membrane material (chemical and automotive industries), textile industry (as PLA fibers), and medical applications. • Packaging material. Biodegradable polymer. • Biodegradable composite.	[124,138,208–214]
Starch/nanocellulose/PLA/PBS	• Excellent impact strength, high thermal stability, and good chemical resistance	• Food packaging	[215,216]
Starch/PVA/Nanocellulose	• High mechanical performance. PVA/starch blends with the addition of 5% (v/v) of nanocellulose exhibited best combination of properties	• Food packaging	[217]

Table 2. *Cont.*

Blend	Properties	Applications	References
Starch/PBSA	• Good mechanical properties, biodegradability, melted processability, and both thermal and chemical resistance	• Antimicrobial packaging materials	[211]
Starch/PHB	• The tensile strength was optimum for the PHB/starch blends ratio of 0.7:0.3 (wt%/wt%)	• Biomaterial in medical applications	[218]
Starch/nanofibre	• Renewability, biodegradability, high mechanical strength, as well as low density and high economic value.	• Transparent materials • Stretchable photonic devices. • Conductive materials. • Wound diagnosis/biosensor. • Scaffolds.	[219–222]
Starch/natural rubber	• Improves the water-resistance • Improves the flexibility of the product • Increases the density of the foam	• Starch forms used for packaging	[223]
Starch-based foam processes/fiber/fillers/resins	• Biodegradable • Improves the functional properties	• Starch forms for food containers • Loose-fill packaging material	[224–226]
Starch-based controlled-release devices	• Biodegradable	• Controlling parasitic mites in honeybee colonies	[227]
Chitosan-starch beads	• Could be a viable alternative method to obtain controlled-release fertilizers	• Controlled release of fertilizers	[228]
Starch/Charcoal/Urea	• Could be a viable alternative method to obtain controlled-release fertilizers	• Controlled release of N fertilizers	[229–231]

4. Biodegradability of Starch and Starch Blends

Fossil-derived plastics take more than 100 years to break down in the environment [232]. Even though various plastic waste-management systems have been proposed for mitigation, execution is somewhat challenging in plastic recycling, incineration, and disposal into landfills at the end of their service life. Mismanaged plastics create adverse impacts on the environment due to the generation of pollutant gases and toxic substances such as dioxins, furans [233], and endocrine disruptors [234], along with the production of leachate consisting of heavy metals that pollute water and soil. As a result, there is an alarming necessity for biodegradable plastics and expanding investigations on understanding the biodegradation pathways of biopolymers [235,236]. Petrochemical plastic production is over 400 million tons as of 2020 [237], and global bioplastic production is expected to exceed 7.5 tons in 2026 [238].

It is crucial to evaluate the biodegradability of agricultural polymers before using them in various processes and industrial applications. The American Society for Testing and Materials (ASTM), the European Committee for Standardization (EN), and the International Standards Organization (ISO) have established standardized tests to assess biodegradability and the degree of biodegradability of polymers [239,240]. Aerobic and anaerobic digestions are the main methods to define biodegradation assays and microbial activity that impact the decomposition rates into environmentally friendly components such as carbon dioxide, methane, water, biomass, and inorganic elements (sodium, potassium, phosphorous, and calcium) [241]. Another biodegradation assay evaluates ecotoxicity in various plants and animal species such as cress and earthworms [240]. Moreover, other standard methods evaluate biodegradability by using material exposure to specific microorganisms [242]. Such methods may be subjected to at least one or a few of the following evaluation methods of samples after the assay [240]: (a) molecular weight, (b) molecular weight distribution, (c) carbon dioxide and/or methane, (d) weight loss of the material, and (e) the visual observations of changes. In addition to the aforementioned items, different analytical techniques can be used to assess biodegradability, such as Fourier transform infrared spectroscopy, differential scanning calorimetry (DSC), nuclear magnetic resonance spectroscopy (NMR), X-ray photoelectron spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray diffraction. After the biodegradation, the tensile properties of polymers (tensile strain, tensile strength, elongation, and tensile modulus) are evaluated before and after comparison [242].

The degradation of starch and starch blends under natural conditions is a complex process that may be facilitated by water adsorption, hydrolysis, and polymer biodegradation [243,244]. There are three stages involved in biodegradation: biodeterioration, biofragmentation, and assimilation [245]. In soil and natural conditions, biodegradation is promoted by microorganisms and enzymes. Complete justification must be given to blends, composites, and surface-modified biodegradable materials due to the tendency to behave differently in biodegradation (Figure 9).

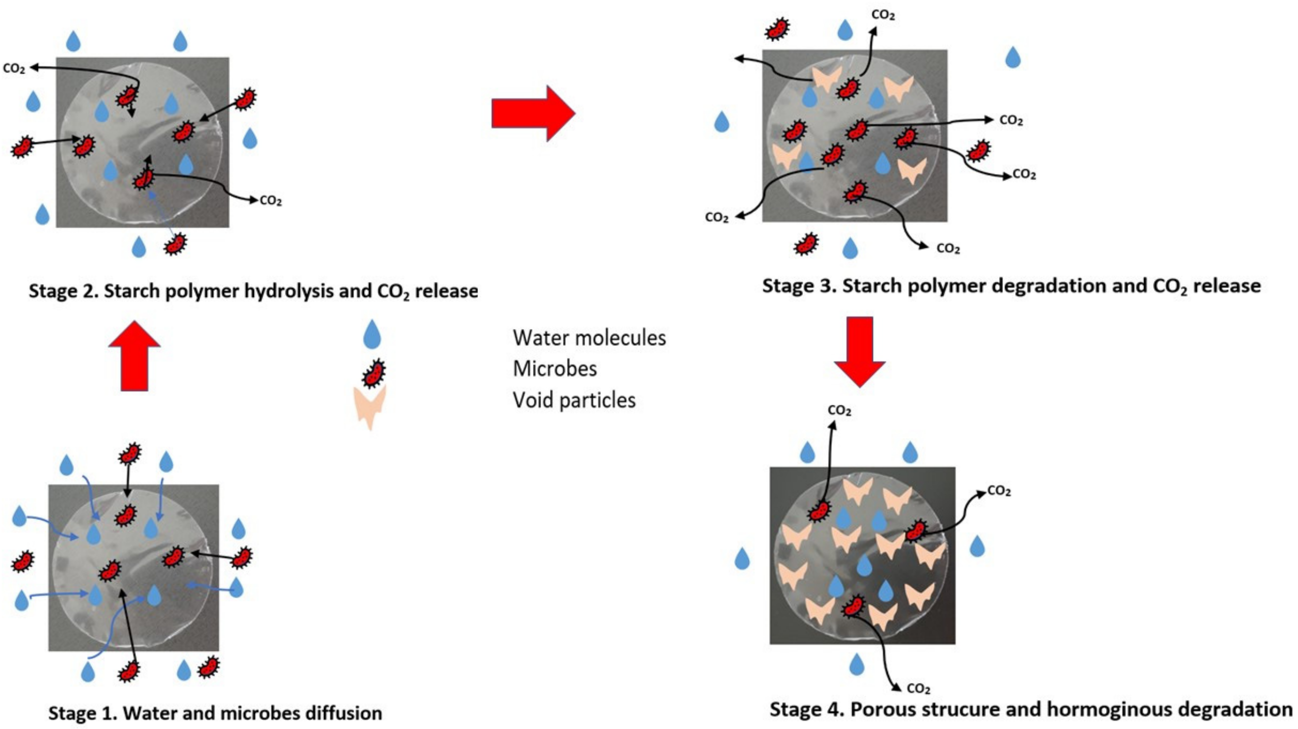

Figure 9. Degradation of biodegradable cassava starch film in soil.

4.1. Biodegradation of Starch/PVA

Starch/PVA blends are of great importance in packaging and agricultural applications due to their high compatibility and excellent film properties [241]. Several studies have been conducted to investigate the biodegradability of starch/PVA blends while preparing various wheat starch/PVA/glycerol blends following the solution cast technique in complying with ISO 14855; they studied composting under degradation for 45 days. After allowing the blends to compost for 45 days, it was observed that starch and glycerol were degraded, leaving the PVA fraction intact. Moreover, the blend characteristics were enhanced without interfering with the biodegradation of starch from surface modification with chitosan [242]. Another study evaluated the biodegradation of PVA/starch blends using a 180-day assay and explained the biodegradation in terms of the changes in molecular weights. These blends had various amounts of cross-linked starch (CLS) compared to PVA blends with acid-modified starches (AMSs).

In similar research, the biodegradation of PVA/AMS blends improved with the increase in AMS percentage. PVA/AMS samples demonstrated a higher degree of biodegradation than PVA/CLS blends [243]. Degradation properties of blow molded PVA/starch films in aqueous anaerobic digestion were studied using sludge from municipal wastewater treatment. This study highlighted that the degradation of PVA blended with native or plasticized starch was significantly increased in terms of degradation rate and elevation, even at a low starch level of 5 wt% [244]. Furthermore, the study reported a higher degree of biodegradation, up to 60%, with loading starch from 21% to 42%, and mechanical properties of starch-modified PVA were declined. Other studies further assessed the anaerobic degradation of glycerol-plasticized and biopolymer such as starch, gellan gum, and xanthan [245].

Parallel research has further evaluated the biodegradability of some starch/PVA-blended films in soil environments using a 6-month soil burial test in which the weight loss over time was measured [246]. The results showed a better degradation of the citric acid-added films than those with glycerol added, and 80% of the total film degradation occurred with an increasing degradation rate while the rate of degradation was slow [246]. This research revealed that the biodegradability of starch/PVA-blended films that incorporated glacial acetic acid (crosslinking agent) in moist soils might take up to 30 days. Research explains that the biodegradation rates of PVA-blended films were governed by moist vs. dry soil and the molecular weight (31 × 103 to 205 × 103 g/mole). It has been reported that degradation was initiated within 3 days in the moist soil, while in dry soils the initiation time of biodegradation increased from 10 to 14 days [247]. The effect of starch content on biodegradability starch/PVA films prepared using melt processing was further discussed in recent research [248]. In this study, the evaluation was carried out by determining the weight loss of specimens buried in soil for 30 days. With increasing starch fraction, the weight loss increased under the same burial test conditions as the highest value of weight loss of the films was obtained at the highest loading of starch in blends. Other researchers affirm the same trend that loading starch in PVA-blended films favors the biodegradation rate; up to 28% to 38% increase in biodegradation rate was achieved at 0–30 wt% loading of starch in PVA blends tested from soil burial method for 45 days [249].

Blends of starch/PVA films from solvent casting resulted in higher susceptibility towards enzymatic degradation in both soil and compost with increasing corn starch loading, which led to achieving up to 85% increase in biodegradation when the burial time is extended in both soil and compost for 8 weeks [123]. The same research further justified that the strength of the blends decreased as the percentage of corn starch was increased. It has been reported that microorganisms from different sources can degrade starch/PVA blends at various degradation rates. Bacteria and fungi species isolated from municipal sewage sludge successfully digested starch components, the amorphous regions of PVA, plasticizer in starch/PVA blends, and glycerol [242]. In similar contexts, two fungi species *Penicillium* and *Apergillus flavus*, isolated from aerobic compost, were able to digest PVA/starch films, resulting in nearly 71% weight loss after 300 days [250]. The same study describes that when two of these fungi activated separately, a higher degradation rate was observed, up to 60% in the actual compost over the same period. Parallel investigations have been executed to assess the biodegradability of PVA/starch blends that have undergone modifications. Fibrous composites of PVA and natural lignocellulosic fibers from orange wastes incorporated with and without cornstarch biodegraded within 30 days in the soil in 80% mineralization [251]. It has been reported that PVA degradation was enhanced with the addition of fibers while both starch and lignocellulosic fiber degraded faster than PVA.

In contrast, nanoparticles may have a lower impact on the biodegradation of composites. A study concludes that in nano-SiO_2-reinforced starch/PVA nanocomposite films, the nanoparticles have no significant effect on the biodegradability of the films as the reference films prepared (without nanoparticles) resulted in a total weight loss of up to 60%. Biodegradation of metaphase films prepared from clay/starch/PVA has been reported to depend on the characteristics of nanoparticles in a composite, such as the type, content, and composition [113]. Some studies represent that the starch/PVA blends are not readily biodegradable and subjected to exposed environmental conditions. This fact can be supported by the following comparative research, which indicated the achievement of a certain degree of biodegradation in solvent-casted starch/PVA films exposed to manure soil. This study further confirmed the similar trend observed in other studies, obtaining a significant increment in biodegradation rate with the increase of the starch content. Moreover, the ultimate weight loss obtained from starch/PVA films did not exceed 40% over three months, confirming that starch/PVA blend films are not easily biodegradable in natural conditions [252]. In contrast, it was also reported that the rate of degradation increased with the addition of starch in a study that followed China National Standards (CN:14432). This study analyzed the biodegradability of starch/PVA blends using bio-reactivity kinetic models. According to first-order kinetics, the microorganism's growth rate increased with the loading of more quantity of starch in blended film preparation. Thereby, the decomposition rate of the the starch/PVA blend reached only around 36.66% after 180 days. It is conclusive that starch/PVA blends may not undergo complete biodegradation within a short period under natural environments [243].

4.2. Biodegradation of Starch/PLA

Following ISO methods, the biodegradability of co-extruded starch/PLA blends in different environments such as liquid, inert solid, and composting media were studied. In the given ISO method, the minimum required mineralization percentage for a compound to be classified as a biodegradable compound is 60%. Concerning starch/PLA blends, it was reported that the percentage of mineralization was higher than 60% and found that starch/PLA blends can be considered biodegradable. Furthermore, this research highlighted that the rate of biodegradation is enhanced with the addition of starch in the liquid medium [253]. In contrast, another study used the standard procedures described under ASTM D 5209–92, 5338–92, ISO/CEN 14852, and 14855 to measure the biodegradability of the starch/PLA films which were exposed to ultraviolet light at 315 nm prior [190]. This study reported that the numerical values of the results are independent of the procedures applied in stage two as the results showed the biodegradation rate was higher when in the liquid medium, 92.4–93.4%, compared to the inert medium, 80–83%. These results make strong inferences with the two-step biodegradation study of agricultural co-extruded starch/PLA mulch films [254].

Biodegradation of PLA blends with starch and wood floor was studied following the ISO 14855 standard for compost. Biodegradation rates of this study were increased by about 80% by increasing the starch loading up to 40% and were discovered to be relatively lower than those of pure PLA compared to starch/PLA and PLA/wood flour blends [255]. The compostability of pure PLA was further researched using starch/PLA blends at different loadings of starch. Based on the visual inspections, it was observed that all the test samples were completely biodegraded without leaving any residue after 30 days [256]. The same study justified the environmental impact and safe use in the ecosystem by ecotoxicity test of pure PLA and starch/PLA blends. Another group of researchers studied the biodegradation and degradation rates of the PLA–starch blends using cellulose as the control material in a controlled environment. PLA blends that incorporated chemically modified TPS (CMPS) were extruded, and within 42 days the biodegradability of the blends increased with increasing CMPS content in the blends, and neat CMPS was fully degraded [257]. The degradation of PLA and TPS blends in simulated soils was further investigated using stimulants such as tert-butyl hydroperoxide, myoglobin, and peroxide-activated myoglobin, in which TPS enhanced the degradation of degradation blends in all systems [258]. Several studies have been conducted using PLA together with starch and different compatibilizers or other substances to evaluate soil biodegradation kinetics and rate. Injection-molded tensile specimens prepared using various combinations of native cornstarch, PLA, and polyhydroxyester-ether (PHEE) were buried in soil for one year to assess the effects of starch and PHEE loading on biodegradation rate [205]. It was reported that the weight loss elevated with increasing starch and poly (hydroxyester-ether) (PHEE) loading in blends [205]. In a comparison study of PLA/starch blends vs. PLA/acrylic acid (AA) grafted starch composite (PLA-g-AA/starch), within 3 months, the starch in the composite was able to entirely degrade in the soil environment [259]. Loading more starch onto composites, the tensile strength at the breakpoint decreased and PLA-g-AA was not degradable as there was not a significant weight observed within 7–12 weeks [259]. Maleic anhydride (MA) has been used as an efficient compatibilizer for PLA/starch blends. The results demonstrated that MA compatibilized blends show better biodegradability than the reference starch/PLA blends in which biodegradability was indicated to be increased with the loading of more starch [260]. A similar study justifies the biodegradability of neat PLA and corn starch/PLA composites with/without lysine di-isocyanate that was examined following enzymatic degradation using Proteinase K and burial tests. According to the results, the degradation rate increased by incorporating more corn starch, and all the corn starch/PLA composites were gradually degraded over the given time period, except pure PLA [261]. In contrast, based on a five-month soil burial experiment designed to interpret the effects of adding PEG to PLA/TPS blends on biodegradation, the mixing of PEG gave an elevated degradation rate, a considerable change in weight loss, and improvement in mechanical properties. It is worth noting, further, that the degradation of blends was increased by incorporating more TPS. It was observed that blends with PEG showed more significant weight loss and enhanced biodegradation of TPS/PLA blends [136].

4.3. Biodegradation of Starch/PCL Blends

Modern research has conducted numerous experiments to evaluate and examine biodegradation and properties of starch/PCL blends. Biodegradation of starch/PCL blends was evaluated from weight loss and the amount of adipic acid immersed from PCL in two types of starch/PCL blends which are distinguished from the starch sources dried granulated sago starch and undried thermoplastic sago starch (TPSS). The biodegradation rate was enhanced by loading more sago starch, indicating a positive trend in mechanical and biodegradation properties in dried granulated sago starch added to PCL blends. Adipic acid liberation is a direct indication of PCL degradation. Granulated sago starch blends liberated more adipic acid as PCL and TPSS decreased biodegradability [262]. Different aerobic environments such as activated sludge and compost, in the presence of *Pseudomonas putida*, the biodegradation of three different types of films formulated from 100% PCL, a blend of 50% modified starch with 50% PCL, and a blend of 50% unmodified starch with 50% PCL blends were studied. Based on the results, there is no significant impact on degradation by *P. putida*. At the same time, considerable deformation in every film was observed within the first 7 days—in both activated sludge and compost the environment may accelerate biodegradation—and after 15 days, all the films had completely degraded [263].

Another study investigated the biodegradability of PCL blends with various starches in anaerobic aqueous environments specific to mesophilic sludge from municipal wastewater treatment [264]. In this study, native corn starch, genetically modified corn starch, gelatinized corn starch, and amaranth starch were used to prepare PCL blends. Then properties of these films were compared with a series of starch/PCL blends that incorporated glycerol. The results demonstrated that the blends that contained glycerol showed better mechanical properties and a higher degree of biodegradation. The biodegradability of the starches may range between 70% (maize starch) and 81% (amaranth starch), while the biodegradation of PCL was reported to be very low, only up to 2% [264]. Other studies assessed the biodegradation of metaphase PCL/starch blends included in various components under compost and soil burial tests.

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Biodegradability-modified PCL following the reaction melt processing using glycidyl methacrylate (GMA) and benzoyl peroxide were studied using the compost method [265]. Two types of blends were not significantly degraded after 8 weeks, while higher degradation was achieved in the blends with lower GMA content. The application of azodicarbonomide (ADC) has been studied in simulated soil to accelerate the biodegradability of PCL/corn starch blends. Various proportions of ADC were incorporated into pure PCL and PCL/cornstarch (50/50) blends [204]. The study reported minimal or no significant weight loss and measurable degradation reported only after 100 days [266]. Compared to pure PCL, the highest biodegradation was recorded in the 50:50 PCL/cornstarch blend. ADC showed no impact on the biodegradation of the blends, which might have inhibited the biodegradation of pure PCL [267]. Another study [268] used three types of PCL blends, high amylose starch [269], and CAB, to evaluate the biodegradation rates. Inside a mature compost made from autoclaved municipal solid wastes, these three blends were buried in a compost seed mixture of compost made from garden waste, which showed the degradation decreased with the decreasing of starch content [268]. The biodegradability of melt-blended PCL/corn starch nanocomposites that had introduced fatty hydroxamic acid to modify sodium montmorillonite (Na-MMT) was studied under the ASTM D5338-92 standard, which reported a higher degree of weight loss after 60 days in PCL nanocomposites than PCL/CS blends [269].

Another team studied various blends of TPS/PCL and PCL modified with an added MA compatibilizer in a soil environment after 21 days and reported that pure TPS was fully degradable. The rate of degradation was elevated with increasing TPS loading in the blend. The lowest biodegradation rate was demonstrated in the blend, which contained 5 wt.% of PCL-MA, and it was further concluded that the rate of biodegradation is independent of the TPS quantity [270]. Sisal fiber-reinforced PCL/starch blends were evaluated over 9 months using the soil burial test to evaluate biodegradation. Results indicate that the biodegradation was increased by adding fibers into starch/PCL blends [271]. Moreover, the researchers also investigated the biodegradation of twin-screw extruded TPS/PCL blends with 5% and 10% of sisal fiber loading and reported that the degradation declined with the incorporation of fibers in blends. At the same time, higher proportions of TPS could enhance the biodegradation of PCL. Furthermore, degradation kinetics of co-extruded TPS and TPS/PCL blends with introduced sisal whisker loadings of 5 and 10 wt.% has been studied. As per the findings, the addition of the whiskers improved the biodegradation of the TPS and the TPS/PCL matrices; also, PCL in TPS/PCL blends accelerates the biodegradation of TPS [272]. Sisal fibers may retard the biodegradation, and the fibers slowed down the biodegradation. Hence, incorporating fibers should be done under many considerations such as application, matrix, and loading level.

4.4. Biodegradation of Starch/PHB-V

Limited studies have investigated degradation kinetics and biodegradation of starch/PHB-V blends using a soil compost test that varied the temperature between 100 °C and 140 °C. These blends were tested for 192, 425, and 600 h to induce thermal aging of extrusion-blended corn starch with poly(3-hydroxybutyrate)-co-poly(3-hydroxyvalerate) (PHB-V) or PCL. Biodegradation of starch/PHB-V at 25% starch loading of the starch impacted thermal aging while demonstrating a higher biodegradation rate within ten months compared to PCL blends. Moreover, the biodegradability of the starch PHB-V blends was increased by loading 50% of the starch into PHB-V, making its degradation time half of that of the PHB-V blend without starch [133]. Three types of TPS blends with potato starch, corn starch, and water-soluble potato starch were used in a similar study with two degrees of gelatinization of PHB under the soil burial test. The results indicate that weight loss decreased as PHB loading increased. In addition, weight loss increased as time and the glycerol content increased [273]. The biodegradability of melt-blended 1:1 PHB-V, and glycerol-TPS with m-MMT were investigated following the soil burial method [274]. The results justified an enhancement of mechanical properties in the blends in comparison to pure TPS and a faster degradation rate than pure PHB/V. Furthermore, biodegradation was accelerated up to 90% with increasing m-MMT loading in blends [274].

4.5. Biodegradation of Starch/PBS and Starch/PBSA

Aerobic and anaerobic biodegradation of cornflour/PBSA and plasticized blends indicated that the biodegradability of blends decreases with incorporating PBSA [139]. In contrast, PBS/starch, PBS, and PLA biodegradation rates were further examined using powdered bioplastics from the soil burial method. According to the observations, the physicochemical structures of PBS and PBS/starch were comparatively more favorable for biodegradation than PLA under the same given test conditions. PBS/starch blends demonstrated the highest degradability and degradation rates, faster in PBS and PBS-starch than neat PLA [275].

4.6. Biodegradation of Ternary Blends

Limited research has been published on the biodegradation of ternary blends. The biodegradability and kinetics of TPS blends of PLA, PCL, and starch were explored. These blends were melt-blended and formulated by introducing acrylic acid grafted by melt blending. As per the results, these blends were rapidly degraded within the first 8 weeks under given soil burial test conditions [141]. Biodegradation of binary and ternary blends of PLA, TPS, and glycidyl methacrylate grafted poly (consider ethylene octane) was assessed following compost testing in complying with ISO 14855. The results indicate that the samples with 40% starch loading underwent more than 80% biodegradation within 10 weeks, compared to blends with 10–20% starch loading, which can only degrade up to 40% under given test conditions. Furthermore, higher biodegradation rates were observed in the blends with GPOE compared to those without GPOE [276].

5. Conclusions

Exponential population growth, geopolitical shifts, scarcities, and supply-chain crises have increased agricultural demand for plastics and cost per hectare. Hence, plastics are extensively used for diverse applications in modern agriculture in every stage of crop production, post-harvesting, greenhouse covers, soil mulching, silage covers, and packaging. In the past two decades, there has been growing environmental awareness provoked by excessive post-consumer wastes and mismanaged plastics and their incorrect disposal. Thereby, sustainable green solutions for agriculture and hunger management are the main challenges in modern agronomics. Starch is one of the most abundant polysaccharides from renewable sources, and the utilization of starch for agricultural applications is contingent. However, the extreme brittleness and hydrophilicity of starch must alter for extended applications in agriculture through chemical, physical, and enzymatic processing. Blends, composites, surface modifications, and nanomaterials deliver favorable chemistries for property enhancements of starch (physicomechanical and barrier performances) and cost reduction in biodegradable polymers. Biodegradable starch blends/composites are a sustainable, eco-friendly alternative for extensively consumed commodity polyolefins (polyethylene, polypropylene) in agriculture. Mechanical properties of biodegradable starch blends declined in many blends as the biodegradation rate in the soil increased at higher starch loading, indicating that starch accelerates the biodegradation of blends with minimum impact on mechanical properties. Hence, starch blends of biodegradable plastics must be encouraged concerning their positive environmental and cost-saving benefits for sustainable and commercially viable modern agricultural solutions.

This review discussed the extent of applicability and property enhancements of starch-based solutions for agriculture. However, the techno-commercial viabilities of given solutions must be validated by their efficiency in manufacturing, scalability, production, appropriateness for application, biodegradation, ecological impact, and post-consumer waste management. The futuristic demands for biodegradable polymers in agriculture and their contribution to global sustainability have inspired many studies and developments.

Starch-based plasticulture would contribute promising value propositions for a circular economy toward sustainable green plasticulture in agriscience.

Author Contributions: Writing—original draft, A.G., A.L., A.M., S.M. and O.M. Review and editing: A.G., A.L., A.M., T.M., S.M., O.M. and C.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors gratefully thank Priyantha Kumara, Nathasha Kodikara and W.M. Thevin Randika for photos.

Conflicts of Interest: The authors declare no conflict of interest.

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