



Review

# Compatibilization of Starch/Synthetic Biodegradable Polymer Blends for Packaging Applications: A Review

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**Abstract:** The health and environmental concerns of the usage of non-biodegradable plastics have driven efforts to explore replacing them with renewable polymers. Although starch is a vital renewable polymer, poor water resistivity and thermo-mechanical properties have limited its applications. Recently, starch/synthetic biodegradable polymer blends have captured greater attention to replace inert plastic materials; the question of ‘immiscibility’ arises during the blend preparation due to the mixing of hydrophilic starch with hydrophobic polymers. The immiscibility issue between starch and synthetic polymers impacts the water absorption, thermo-mechanical properties, and chemical stability demanded by various engineering applications. Numerous studies have been carried out to eliminate the immiscibility issues of the different components in the polymer blends while enhancing the thermo-mechanical properties. Incorporating compatibilizers into the blend mixtures has significantly reduced the particle sizes of the dispersed phase while improving the interfacial adhesion between the starch and synthetic biodegradable polymer, leading to fine and homogeneous structures. Thus, Significant improvements in thermo-mechanical and barrier properties and water resistance can be observed in the compatibilized blends. This review provides an extensive discussion on the compatibilization processes of starch and petroleum-based polymer blends.

**Keywords:** thermoplastic starch; synthetic biodegradable polymers; compatibilizer; mechanical properties; surface properties; biodegradable films

## 1. Introduction

Due to the rapid industrialization and urban development across the globe, the usage of petroleum-based inert plastics has been drastically increased [1–3] in daily life, the biomedical field, agriculture, and in the food industry [4,5] owing to their low cost, lightweight [6], strength to weight ratio, easy processability, durability [6–8], improved barrier properties, and heat stability [9]. However, the tremendous increase in the usage and production of petroleum-based plastic materials has resulted in vast amounts of plastic waste on the land sites [1,10] since they take 100–450 years to degrade naturally [11–14].

Apart from the above, it is a well-known fact that non-degradable polymers are derived from petroleum and its allied components [2]. Consequently, the depletion of petroleum resources can occur since the natural resources take millions of years to form and are finite in quantity [15].

Although, at present, numerous ways of managing polymeric wastes are introduced, including incineration, recycling, and energy recovery systems, incineration in landfilling sites may lead to the release of heat and unacceptable emissions of harmful compounds, such as greenhouse gases and volatile compounds, into the atmosphere [16,17]. In contrast, the recycling process is rarely used due to the consumption of a considerable amount of thermal energy, the complexity of design, and relatively high cost, reducing the process sustainability [9,18]. Thus, waste plastics are eventually destined to be burnt or buried in landfill sites [9]. Therefore, disposal problems, strict regulations on plastic use, new criteria for a cleaner and safer environment [13,19], and the global shortage of petroleum resources have driven the development of biodegradable and renewable materials [11,20,21] as alternatives to replace or reduce synthetic plastics.

Generally, single-use plastic materials used in food packaging applications, personal care products, agricultural purposes, and fishing equipment are released directly to the environment [22]. Therefore, it is conclusive that recycling is not practicable and economical for single-use plastics [23]. Furthermore, due to the depletion of petroleum resources and environmental concerns, the development of environmentally friendly alternatives to meet the ever-increasing demand for single-use plastics materials, known as 'green materials' [24], has become vital importance. Therefore, many approaches are currently underway to utilize biodegradable polymers as alternatives for non-biodegradable synthetic polymers, minimizing environmental and other commercial issues [25]. Interestingly, starch, as a packaging material, has attracted much attention both in academia as well as the industry [26] owing to its relative abundance, renewability [26,27], biodegradability [27], low cost, easy handling [4], and the capability of dissolving in water [28].

Despite starch's inherent superior properties, native starch cannot be utilized in practical applications due to its ever-increasing brittleness with time in the absence of a suitable plasticizer, poor processability and storage stability, and low mechanical and thermal properties [23,29,30]. Though starch is plasticized to obtain thermoplastic starch (TPS) to improve its properties, TPS alone also cannot be used as a substitute for petroleum-based inert plastic materials due to its poor mechanical and thermal properties, water sensitivity, deterioration of mechanical properties during the exposure to humid environments, poor barrier properties, and plasticizer migration [23,29–34]. Moreover, packaging materials composed entirely of starch lack the strength and rigidity to withstand mechanical stresses. Hence, the solution is to blend starch with a robust support base [1] to widen its range of applications [4]. Therefore, the blending of TPS with synthetic biodegradable polymers has become an attractive pathway to overcoming the major drawbacks of TPS while achieving specific requirements of an application [23].

It is well-known that starch is a hydrophilic polymer since each starch monomer consists of three free hydroxyl groups in its chemical structure [23]. In contrast, synthetic polymers are hydrophobic and thermodynamically immiscible with hydrophilic starch. Therefore, simple mixing of these two polymer components may result in phase separation, phase incompatibility, and poor mechanical properties [30,35]. However, the mechanical properties of polymer blends can be enhanced by incorporating a suitable compatibilizing agent during the blend preparation [31], and this process of stabilizing polymer blends is called 'compatibilization' [36].

Though the immiscible polymer blends are compatibilized using suitable compatibilizing agents, the properties of the blends play a significant role in determining the appropriate amount of the compatibilizer to be incorporated and the polymer ratio in the blends, which provides the required properties for a specific application. Despite the fact that blend features mainly depend on the properties of the individual polymer components present in the blend, the morphology of the blend film is the major factor for producing

polymer blends with enhanced properties [23]. Apart from the morphology, it is said that the crystallinity of the polymer phases also plays a significant role in performing the properties of a polymer blend [24]. Though the phase morphology of starch-based blends is coarse due to starch's high molecular weight, strong hydrogen bonding, and hydrophilic nature [22], a fine morphology is required for the enhanced mechanical properties of a blend [22,24].

Therefore, it is conclusive that the mechanical properties of a certain polymer blend reflect the compatibility between the two polymer phases [37]. Usually, the elongation at break and the toughness of a polymer blend are governed by the domain size of the dispersed phase and the interfacial adhesion between the matrix and the dispersed phase [38]. Apart from the mechanical properties, thermal and barrier properties of a particular blend are also important parameters to be altered during packaging applications [39]. It is a commonly known fact that water is a plasticizer for starch. Water absorption of starch-based blends leads to increased mobility, and the starch molecules tend to reorganize and aggregate themselves. Therefore, any improvement in water resistance in these blends is of paramount importance [40]. Besides, melt flow index (MFI) for a particular polymer blend is also a good guideline during processing [41].

Recent advances have prompted this review on incorporating different compatibilizing agents for starch/synthetic biodegradable polymer blends to improve essential properties associated with packaging applications. Therefore, this review focuses on starch/synthetic biodegradable polymer blends for sustainable packaging applications. Most importantly, the effects of various compatibilization processes on the thermo-mechanical, physical, and functional properties of different polymer blends have also been reviewed.

## 2. Non-Degradable Petroleum-Based Plastic Materials

With the diverse range of innovations in plastic production, they have been employed in many sectors, including packaging, automotive, construction, healthcare, and electronics. Therefore, due to the incremental usage of plastic, plastic waste generation has also increased over the last few decades [12,13,42]. Moreover, the global consumption of plastic products has significantly increased to around 400 million tons [8]. Almost all the plastic materials are made up of polyolefins such as polypropylene (PP), polycarbonate (PC), polyvinyl chloride (PVC), polyethylene (PE), and polystyrene (PS). These synthetic or non-biodegradable polymers are derived from petroleum-based materials [15].

Table 1 depicts the widely used non-biodegradable petroleum-based plastic materials, applications, and their contribution to the solid waste, and recycling percentages. PET is one of the most consumed plastics among those plastic waste due to its intrinsic properties, including scalability, lightweight, and pressure resistivity [43].

**Table 1.** Different types of synthetic polymers and their contribution to solid waste.

Synthetic Non-Degradable Polymer	Applications	Contribution to Municipal Solid Waste	Recycle Percentage (%)	Ref.
Polyethylene terephthalate (PET or PETE)	Mineral water bottles Soft drink bottles	29.1	25	[43]
High Density Polyethylene (HDPE)	Packaging of oil bottles and shampoo bottles	17.6	30–35	[44]
Polyvinyl chloride (PVC)	Cooking oil bottles	12.2	less than 1	[43]
Polypropylene (PP)	Drinking water bottles Plastic odicolon bottles	24.3	3	[44]
Polystyrene (PS)	Disposable dinking cups	35.0	Recycling is comparatively negligible.	[43]

As can be evidenced from Table 1, PET has been widely used in the global plastic market with the second highest recyclability. High-density polyethylene (HDPE) is a long linear polymer chain with a high crystalline structure and low branching, providing high strength properties. HDPE is considered the third-largest type of plastic found in municipal solid waste contributing nearly 17.6% to plastic waste, as shown in Table 1. Moreover, low-density polyethylene (LDPE) is widely used in squeezing bottles. Although LDPE is reusable, they are not always recycled. Therefore, LDPE waste has accumulated to become the second-largest plastic waste in municipal solid waste after PP [44]. PVC is a soft, flexible plastic-type, recycled less than 1% after use (see Table 1). PP is a saturated polymer with a linear hydrocarbon chain with good chemical and heat resistance while being tough and light in weight. According to Table 1, in the US, 3% of PP is recycled. Furthermore, PS is a cheap, lightweight plastic made up of styrene monomers obtained from liquid petrochemicals. The structure of PS consists of a long hydrocarbon chain containing a phenyl group attached to each carbon atom [43].

Table 1 justifies the importance of non-biodegradable plastics in day-to-day lives and current issues associated with the recycling and disposal of synthetic plastics. As shown in Table 1, the highest percentage of plastics is sent for landfilling, occupying a significant space on the land. In Europe, approximately 38%, 26%, and 36% of plastic waste are generally sent for landfilling, recycling, and energy recovery through utilization, respectively [43].

### 3. Biodegradable Polymers

Biodegradable polymers are used for various packaging, building materials, hygiene products, and medical applications, due to their intriguing properties, such as durability, easy processing, and relatively low-cost manufacturing [45]. Biodegradable polymers can be classified according to chemical composition, synthesis method, processing method, economic importance, and applications [46]. Generally, these polymers degrade into final products like water, carbon dioxide, minerals, and intermediate products (biomass and humid materials) in a natural environment [47]. Moreover, biodegradable polymers can be derived from renewable or petroleum resources [23].

Biodegradable polymers are generally categorized into two major groups as natural and synthetic biopolymers based on their origin. Furthermore, according to Avérous and Pollet [48] and Ghanbarzadeh and Almasi [46], biodegradable polymers can be classified into three major groups based on their origin, namely (i) natural polymers, (ii) synthetic polymers, and (iii) modified natural polymers (see Figure 1) [46,48]. Figure 1 shows the schematic representation of biodegradable polymers based on their source of origin.

Interestingly, biodegradable polymers offer tremendous potential uses in many exciting applications, such as drug delivery, tissue engineering, gene therapy, regenerative medicine, temporary implantable devices, food containers, soil retention sheeting, agricultural mulch film, waste bags, and packaging materials. [23,25,49]. Among these diverse applications, the development of packaging materials to address the ever-increasing demand has been significant since plastic materials used in food packaging and other personal care products are mostly single-use. Moreover, natural biodegradable polymers, including chitosan, cellulose, chitin, cyclodextrin, and starch, have recently captured attention due to their low toxicity, biocompatibility, and biodegradability [50–53].

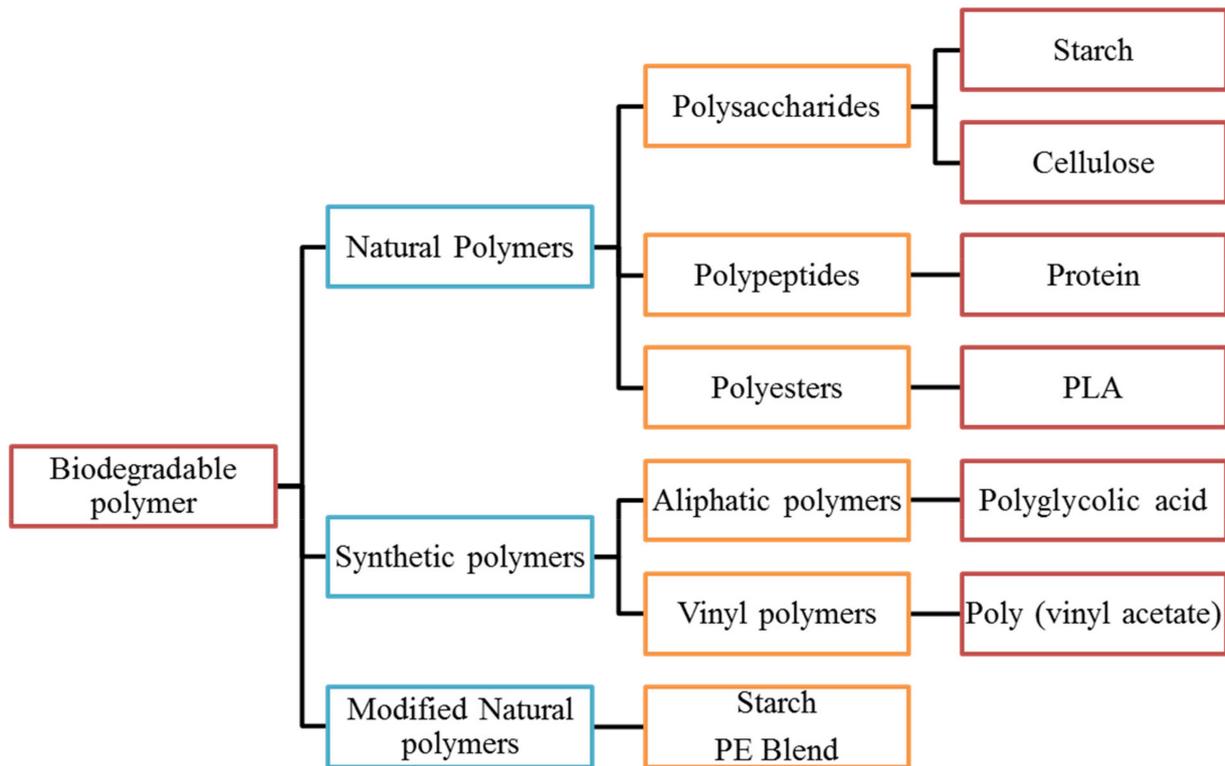
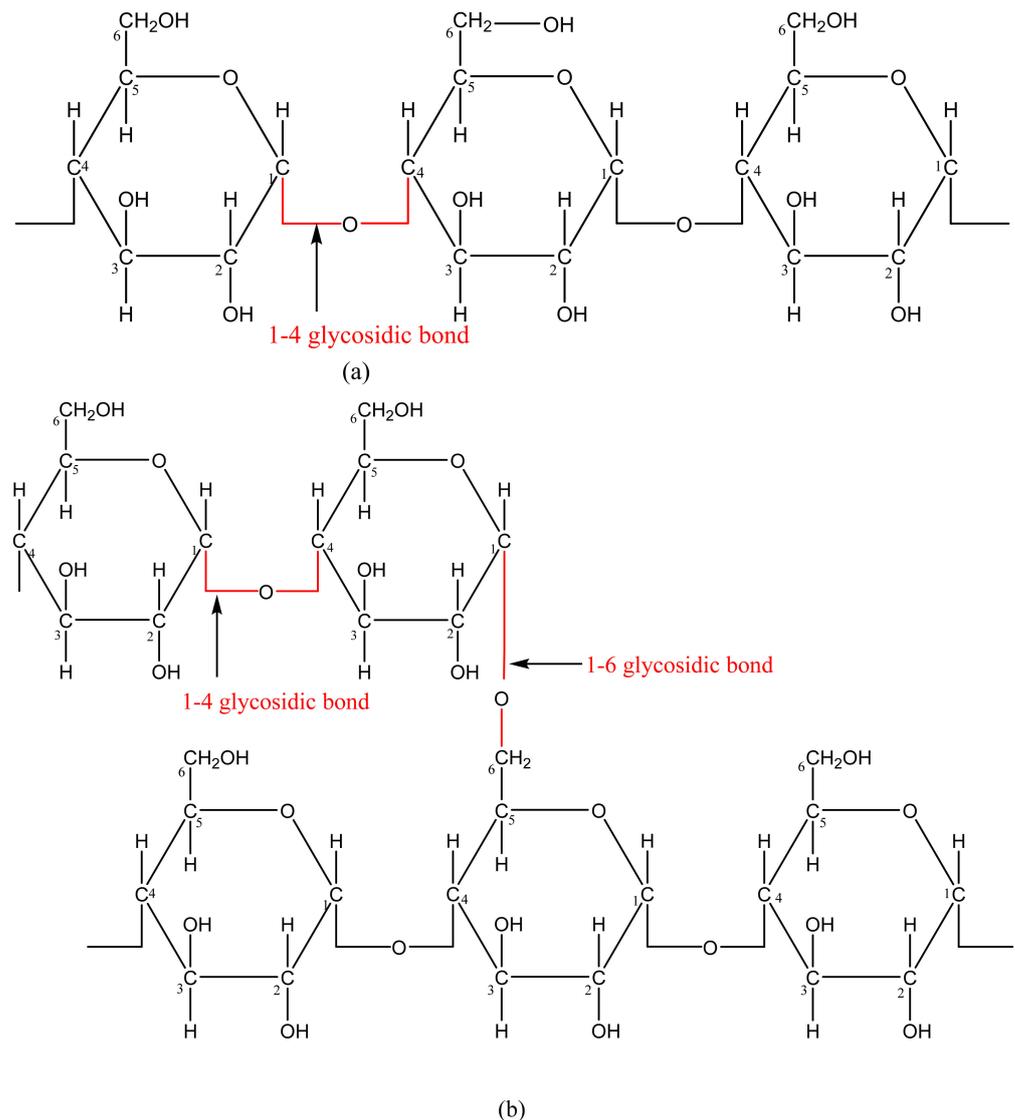


Figure 1. Schematic representation of biodegradable polymers based on their origin [46,48].

#### 4. Starch

Starch, which is the second most abundant [54,55] biopolymer after cellulose [23] and one of the low-cost polysaccharides [56], is a common constituent that can be found in all organs of higher plants. Starch is the major polysaccharide chain that stores carbohydrates. Apart from the higher plants, starch can be found in mosses, ferns, protozoa, algae and bacteria. Starch is widely present in green plants and every type of tissue, including leaves, fruits, roots, stems, shoots, and pollen grains [57]. The main botanical origins of starch production are maize, cassava, wheat, and potato, respectively [58]. Starch content in potato tubers, maize endosperms, sweet potato, and cassava and yam roots varies from 65% to 90% of the total dry weight. Starch consists of two types of polysaccharides, typically known as linear amylose and branch amylopectin [59], as shown in Figure 2. Amylose is composed of D-glucose units linked by 1–4 glycosidic bonds (see Figure 2a) while amylopectin is composed of poly glucose units linked by 1–4 and 1–6 glycosidic bonds [60] (see Figure 2b). Generally, the amount of amylose and amylopectin varies according to the source of origin [57].

Starch was first used extensively in the plastic industry as a filler [61] to produce eco-friendly and low-cost plastic materials [23,62]. However, as a solution for minimizing non-biodegradable plastic materials, starch is used in its plasticized form, known as thermoplastic starch (TPS), to compound with other synthetic biodegradable polymers, subsequently reducing the ‘white pollution’ and carbon footprint [22,62].



**Figure 2.** Chemical structure of (a) Amylose and (b) Amylopectin.

### 5. Thermoplastic Starch (TPS)

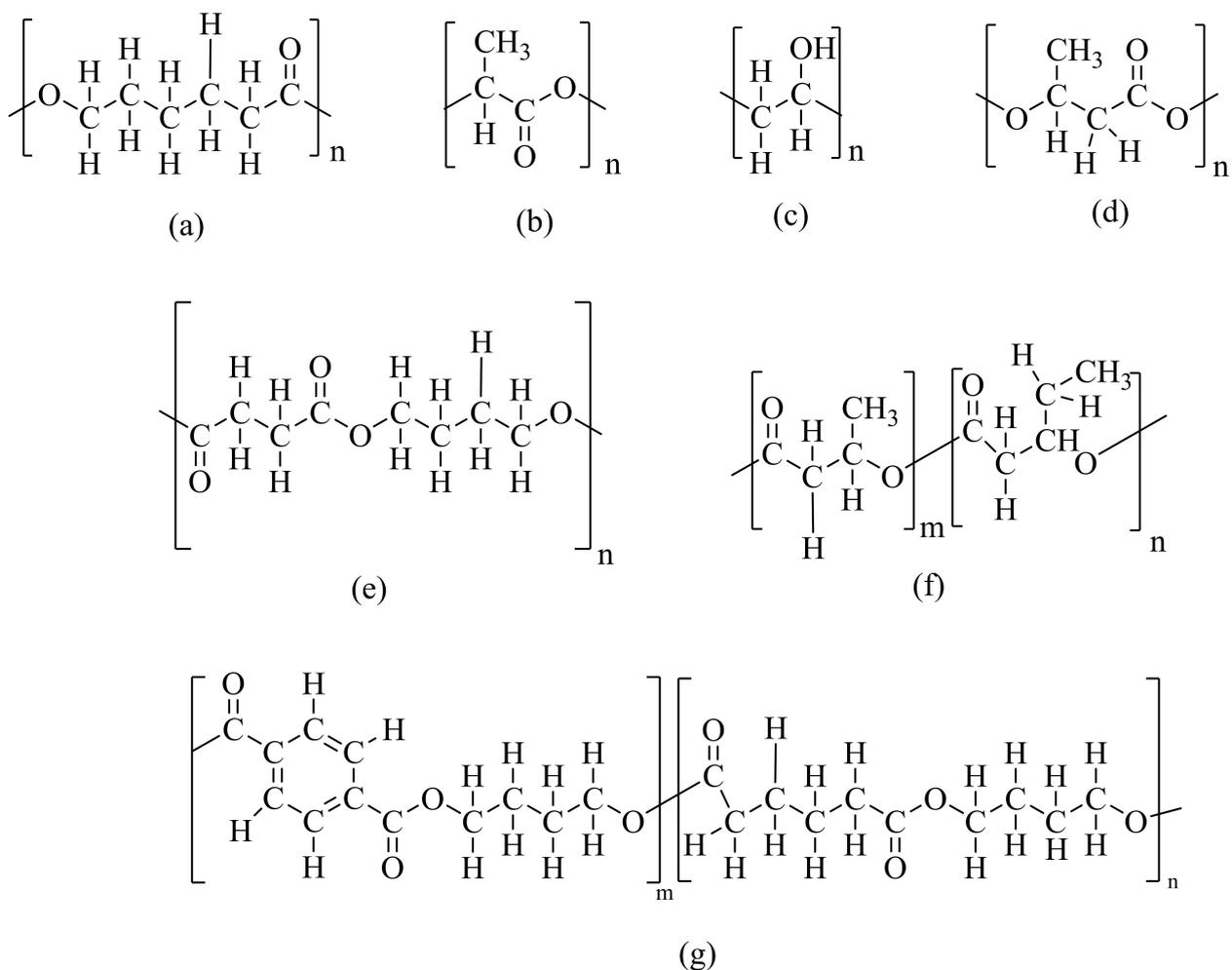
Native starch is not suitable for direct practical applications due to brittleness, low processability and storage stability [23,30,63,64]. Though native starch is considered as a non-plasticized material due to the intra- and intermolecular hydrogen bonds between the hydroxyl groups of starch molecules, starch can be converted into a continuous polymeric entangled phase by mixing with aqueous or non-aqueous plasticizers, including glycerol, glycol, xylitol, sorbitol, sugars, ethanolamine, urea, formamide, acetamide etc. [23]. During the thermoplastic process, in the presence of plasticizers, a semi-crystalline granule of starch is transformed into a homogeneous material via hydrogen bond cleavage between starch molecules, leading to the loss of crystallinity, reduced glass transition temperature of starch, and improved chain flexibility. Finally, petroleum-like TPS polymer with melt processing ability is formed [23,65]. Therefore, when a plasticizer is added to starch, it becomes easier to process than native starch and converts into a moldable material. Most importantly, the properties of TPS highly depend on the amount and the type of plasticizer added [22,23].

Among different plasticizers, glycerol is considered the most widely used due to its low cost, non-toxicity, and high boiling point. According to the literature, both native and modified starch is used in TPS preparation [66]. It is reported that TPS from starch acetates

presents enhanced mechanical properties and reduced hydrophilicity. Moreover, TPS prepared from dialdehyde starch exhibit reduced glass transition temperature, increased mechanical properties and reduced hydrophilicity and water vapor permeability [23]. Although starch is plasticized in the presence of different plasticizers, TPS alone cannot be used as a substitute for petroleum-based inert plastic materials. Therefore, TPS is blended with another biodegradable polymer [23]. The major reasons for blending TPS with synthetic biodegradable polymers are to reduce the cost [22,23,37,40], improve biodegradation rate [40,67], maintain biocompatibility and renewability [22], and achieve acceptable levels of physio-mechanical properties [56]. Therefore, the combination of these two polymer components provides synergetic effects [37].

## 6. Synthetic Biodegradable Polymers

TPS is widely blended with hydrophobic biodegradable polymers, such as polylactic acid (PLA), polycaprolactone (PCL), polyhydroxybutyrate (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polybutylene succinate (PBS), and poly (butylene adipate-co-terephthalate) (PBAT) (see Figure 3) [23]. Figure 3 shows the chemical structures of common synthetic biodegradable polymers. Usually, reactive melt blending is carried out by incorporating an appropriate compatibilizing agent to increase TPS content without severely impacting the mechanical properties while linking the two immiscible polymers through covalent bonds and enhancing the interfacial adhesion among them. This strong interfacial adhesion leads to an effective stress transfer between the two polymer phases [68].



**Figure 3.** Chemical structures of (a) Polycaprolactone (b) Polylactic acid (c) Polyvinylalcohol (d) Polyhydroxybutyrate (e) Polybutylene succinate (f) Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and (g) Poly(butylene adipate-co-terephthalate).

Polycaprolactone, commonly known as PCL (see Figure 3a), is a typical aliphatic polyester that plays a significant role in packaging and medical applications [39,69]. PCL is linear, hydrophobic, partially crystalline, and can be slowly utilized by microorganisms. Moreover, its physical properties and commercial availability make it very attractive as a substitute for non-biodegradable polymers for commodity applications [70]. Due to the properties such as biodegradability, biocompatibility, non-toxicity, and resistance to water, oil, solvent, and chlorine, PCL is highly considered in industries. However, the main limitation of PCL is the low melting temperature which can be overcome by blending with another polymer [70,71]. Among possible blending methods, PCL with starch has become a commodity that reduces moisture susceptibility and enhances thermal and mechanical properties [39].

Polyvinyl alcohol, known as PVA (see Figure 3c), has become one of the widely used and available biodegradable synthetic polymers [72,73], which offers exciting properties, such as good processability, water solubility [72], higher thermal stability [27], good barrier properties [11], easy processability, chemical resistance [19], better mechanical properties [12,14,19,26], non-toxicity [26,74], biocompatibility, and better film-forming and adhesive properties [26]. In addition, PVA is one of the few synthetic polymers produced via hydrolysis of polyvinyl acetate [72], a non-petroleum route [75].

Polybutylene succinate (PBS) is a biodegradable polyester, consisting of bio-based carbon content between 35% and 50% [67], see Figure 3e. PBS exhibits promising properties, such as excellent impact strength, melt processability, biodegradability, high flexibility, good thermal stability, and good chemical resistivity. Moreover, these properties are quite similar to those of polyethylene [37,41,76].

Poly(lactic acid) (PLA) is derived through the bacterial fermentation of annually recyclable plant-based carbohydrates, such as starch, sugarcane, and bagasse, Figure 3b. However, the commercial production of PLA involves condensation polymerization followed by ring-opening polymerization of lactic acid. PLA plays a significant role in the packaging industry since it possesses impressive mechanical, chemical, and gas barrier properties, along with biocompatibility and odorless characteristics [33,77–79].

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), commonly known as PHBV (see Figure 3f), is one of the commercially available biodegradable synthetic polymers produced as a reserve material by numerous microorganisms under limited concentrations of essential nutrients, such as nitrogen or phosphorus, and excess carbon source [80]. Moreover, PHBV is a thermoplastic linear aliphatic polyester produced via copolymerization of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. Although PHBV is a biodegradable, non-toxic, biocompatible plastic capable of serving as a good alternative for many non-biodegradable polymers, its high melting point (>170 °C), high relative crystallinity, brittleness, and narrow processing window have limited its applications [80,81].

Poly(butylene adipate-co-terephthalate), also known as PBAT (see Figure 3g), is generally marketed as a fully biodegradable alternative to low-density polyethylene, consisting of similar properties, including flexibility and resilience, allowing it to be used during the production of plastic bags and wraps. Moreover, PBAT is a synthetic aliphatic-aromatic co-polyester often blended with TPS to improve the drawbacks of plasticized starch, reduce the cost, improve the biodegradability, and enhance the mechanical properties and dimensional stability [82–86].

Polyhydroxyalkanoate (PHA) is a bio-based aliphatic polyester produced by commonly found microorganisms as an energy storage mechanism. Polyhydroxybutyrate (PHB) is a well-known member of the PHAs family [87], see Figure 3d. Although PHB has received much attention due to its renewability, better ultra-violet resistivity, non-toxic nature, biocompostability under both aerobic and anaerobic conditions, PHB is not widely applied alone in industrial applications due to its high cost, poor processability, and brittleness [22,88].

### 7. Major Types of Compatibilization Techniques

There are two types of polymer blends, namely miscible polymer blends and immiscible polymer blends. Miscible blends are characterized by the presence of one glass transition temperature and a single phase. In contrast, immiscible polymer blends are characterized by separated phases, exhibiting the glass transition and melting temperatures of each component at different temperatures [23]. This phase separation can be ascribed to the polarity of the building blocks. This phase separation is unavoidable and significantly limits the applications of these blend films [35]. Moreover, the phase separation occurs when blending TPS with non-polar synthetic biodegradable polymers, providing a high interfacial tension (surface energies) between the polar TPS and the non-polar polymer [69].

There are three major methods of compatibilization of immiscible polymer blends, namely: (i) ex situ compatibilization, (ii) in situ compatibilization, and (iii) dynamic vulcanization, as shown in Figure 4 [23]. Figure 4 illustrates the summary of the compatibilization techniques and their unique features.

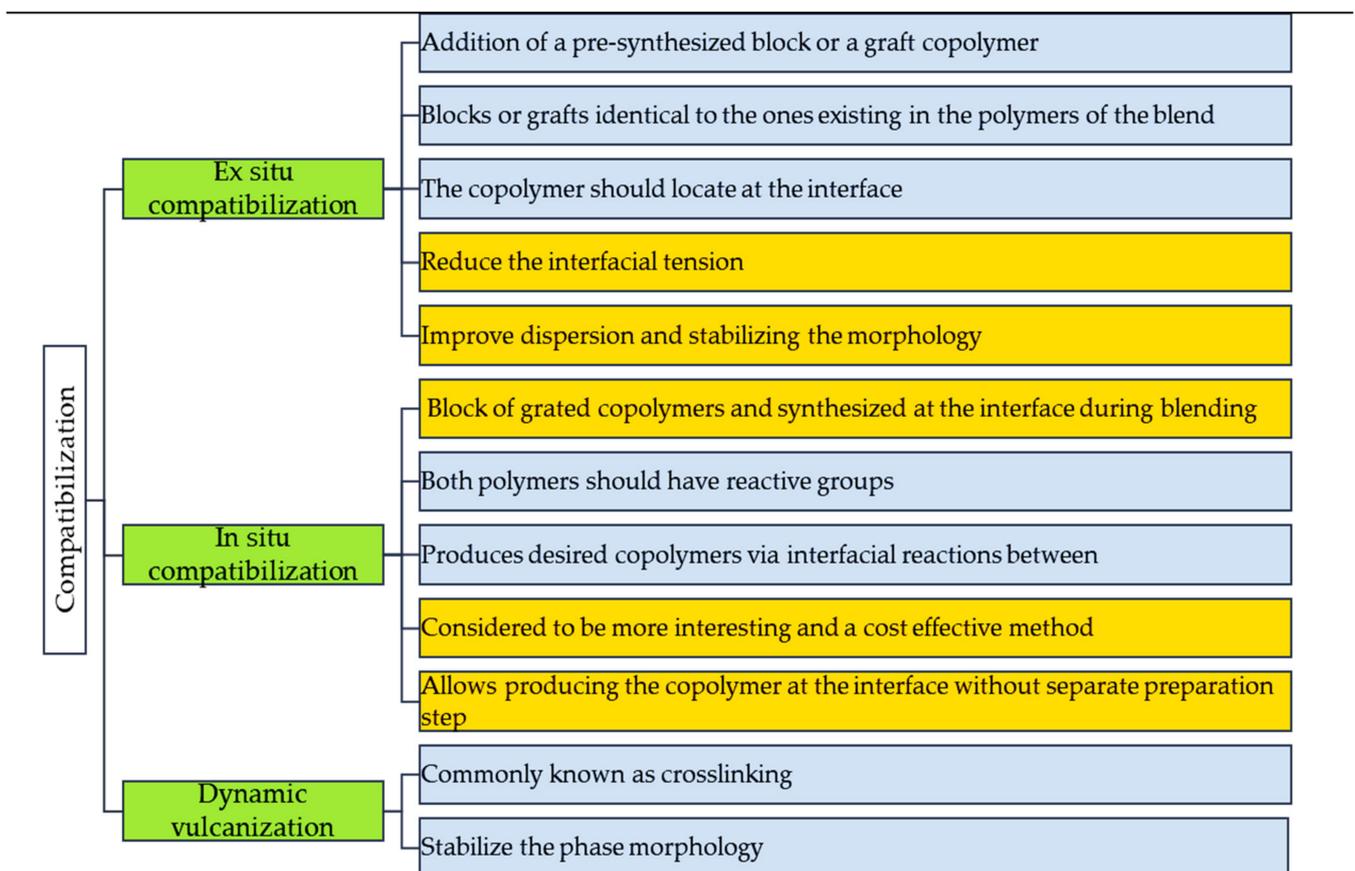


Figure 4. Summary of different types of compatibilization.

According to the literature, only a small amount of compatibilizer is required to meet an immiscible polymer blend [31]. However, the major challenge associated with a compatibilizer is to promote good interfacial adhesion between the polymer phases to achieve the product specifications.

### 8. Preparation Methods of Starch Blends

Different types of starch-based blend preparation methods have been adopted by different researchers, such as solution casting, extrusion, injection moulding, compression moulding, and hot-pressing.

Mani et al. prepared compatibilized starch/PCL blends using a co-rotating twin-screw extruder, while the samples for testing were prepared by either compression moulding or injection moulding [36]. The same method for preparing starch/PCL blends was followed by Ortega-Tora and coworkers [32]. Moreover, Yin et al. [24] prepared compatibilized starch/PBS blends following the same method [24]. Li et al., and Ren et al., prepared starch/PBAT blends and starch/PLA blend sheets using the same method [33,89]. Moreover, the same technique was followed by Magalhaes and Andrade [40] and Ma et al. [22] for preparing starch/PHBV, starch/PLA and starch/PHB blends.

Kim and coworkers used melt mixing with a Brabender mixer and subjected the blended samples to be moulded via hot-pressing [38]. The same procedure was followed by Wang et al. [90] and Liu et al. [91] for preparing starch/PLA blends [90,91]

Both Singh et al., and Sugih and coworkers prepared starch/PCL blends using a mechanical kneader on a two-roll mill, and then the molten composite materials were moulded to investigate the effect of compatibilization [35,70]. Furthermore, Akrami et al. [92] investigated the effect of compatibilization of starch/PLA blended sheets by initially melt mixing with a Brabender mixer, followed by compression moulding [92]. Chen et al., explored the compatibilization effect of starch/PCL blended sheets by mixing the components in an internal mixer and then by hot-pressing [29]. A similar procedure was followed by Collazo-Bigliardi et al. [93] to prepare starch/PLA blends [93].

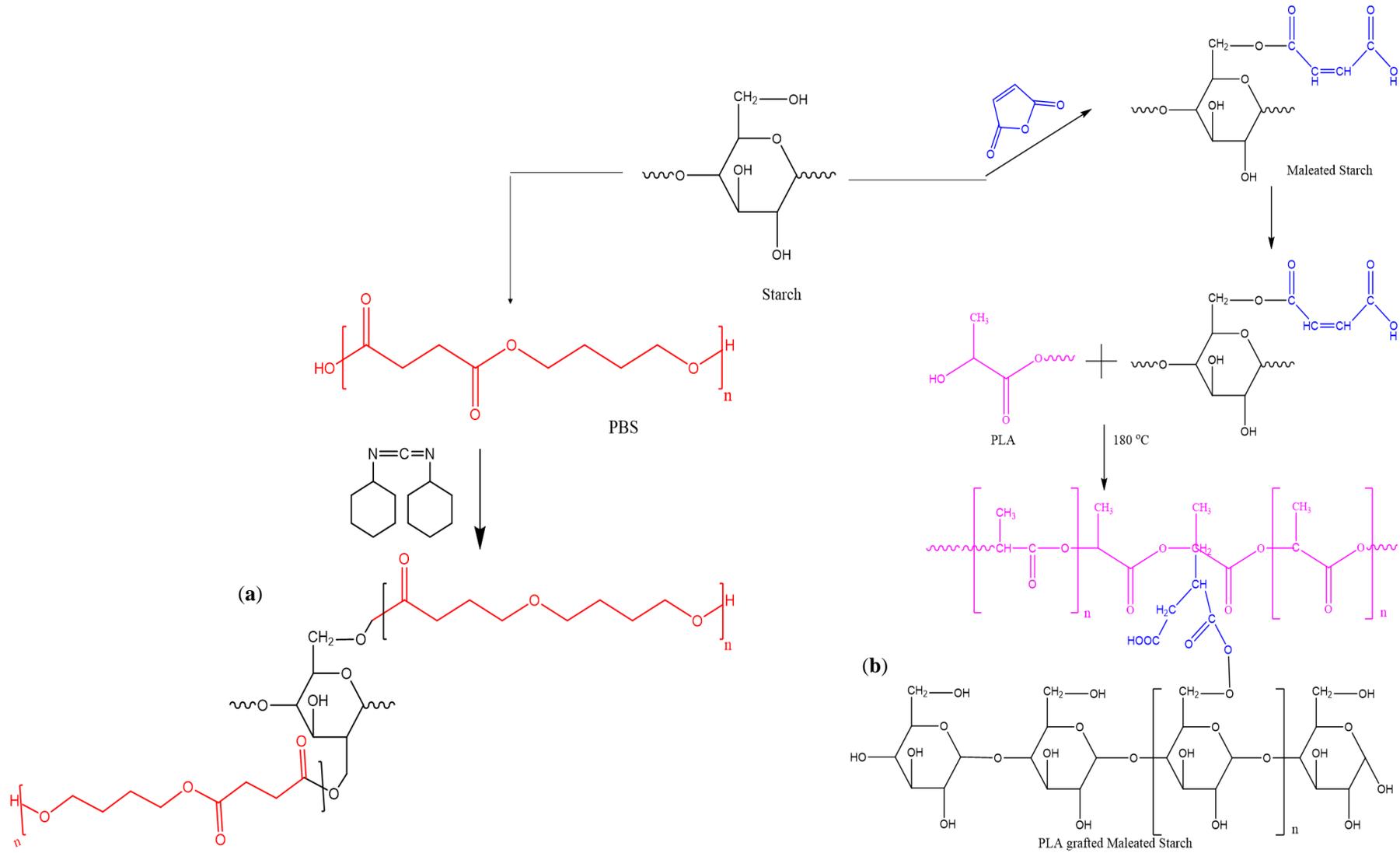
Fahrngruber et al. [67] examined the effect of compatibilization of the starch/PBS blends by preparing the blends via extrusion using a co-rotating twin-screw extruder and subsequently preparing the flat films using a small-scale flat film extrusion line [67].

Starch/PVA blended films have been prepared by solution casting [94,95] to investigate the effect of different compatibilization techniques [96]. The composite films containing PVA/starch/carbon nanotubes were prepared by solution mixing and casting by Jose et al. [56]. The exact process for starch/PVA thin film preparation was followed by Gupta et al. [11] and Widiarto [11,97].

## 9. Synthesis of Compatibilizers

Mani et al. investigated the effect of starch grafted PCL (Starch-g-PCL) as the compatibilizer for starch/PCL blends. Herein, the compatibilizer was synthesized via two steps, namely (i) the isocyanate-terminated PCL was prepared by reacting terminal hydroxyl groups of PCLs with diisocyanate, then (ii) isocyanate-terminated PCL was grafted onto starch through the introduction of urethane links [36]. The authors also reported the effect of polyacrylic acid (PAA) grafted PCL (PAA-g-PCL) synthesized as a compatibilizer for starch/PCL blended films via the copolymerization of a macromonomer named PCL acrylate and acrylic acid [38]. Sugih and coworkers investigated the effect of two different types of compatibilizers for starch/PCL blended sheets, namely (i) PCL grafted glycidyl methacrylate (PCL-g-GMA) and (ii) PCL-g-diethyl maleate (PCL-g-DEM), by reacting glycidyl methacrylate (GMA) or diethyl maleate (DEM) with low molecular PCL and benzoyl peroxide (BPO) as the radical initiator [35]. Ortega-Tora and coworkers [32] carried out a study to overcome the incompatibility between starch and PCL by synthesizing two different compatibilizing agents: PCL<sub>MG</sub> where polar functional groups were chemically grafted on hydrophobic PCL chains by inserting maleic anhydride (MA) and GMA molecules, and (ii) PCL<sub>G</sub> by grafting only GMA onto PCL [32]. Lopez and coworkers developed starch grafted PCL (St-g-PCL) as a compatibilizer for starch/PCL blends. The St-g-PCL copolymer was obtained under vacuum by employing low doses of Co  $\gamma$ -radiation [39].

Yin et al. [24] used MA-g-PBS or rPBS (maleic anhydride grafted PBS) as an interfacial compatibilizing agent to overcome the incompatibility between both starch and PBS [24]. Furthermore, Suchao-in et al. synthesized starch grafted PBS (Starch-g-PBS) as a compatibilizer to enhance the properties of starch/PBS blends. Herein, the synthesis route during the preparation of starch-g-PBS was carried out according to Figure 5a using different molar ratios of PBS to starch for 0.63, 1, 1.5, 2.2, 3.5, and 6 mmol of dicyclohexylcarbodiimide (DCC) [37].



**Figure 5.** Synthesis route during the preparation of (a) Starch-g-PBS (b) PLA-g-MTPS.

Akrami et al. [92] studied the effect of maleic anhydride grafted poly-ethylene glycol grafted starch (mPEG-g-St) as a compatibilizer on mechanical properties and biodegradability in TPS/PLA blend composites. In this study, the synthesis of the compatibilizer was undertaken via two steps. As the initial step, the grafting reaction between MA and PEG (4:40 *w/w* ratio) was accomplished via melt mixing in a flask at 130 °C with 2 h agitation. Secondly, starch particles (56 wt%) were added to the mixture of PEG and MA, and the reaction was continued for another 2 h at 150 °C [92]. Another study was carried out to explore the effect of PLA grafted glycidyl methacrylate (GPLA-x) as the compatibilizing agent on the morphological, thermal, mechanical and medium resistance properties of PLA/TPS. The graft copolymer GPLA-x, which contains a hydrophilic chain, was synthesized from glycidyl methacrylate monomer by free radical initiated (benzoyl peroxide initiator) grafting PLA using a melt polymerization reaction [91].

Wootthikanokkhan and coworkers conducted a study to examine the effect of polylactic acid grafted maleated thermoplastic starch (PLA-g-MTPS) as a compatibilizer in PLA/TPS blends. The PLA-g-MTPS copolymers were prepared by reacting maleic anhydride with TPS, then grafting the maleated TPS with PLA using Luperox101 0.25–1.0 phr (parts per hundred resin) as the initiator [98], see Figure 5b.

## 10. Effects of Compatibilization in Starch/Synthetic Biodegradable Polymer Blends

The following section discusses seven industrially important starch/synthetic biodegradable polymer blends, focusing on different compatibilization techniques.

### 10.1. Starch/PCL Blends

Kim et al., synthesized polyacrylic acid (PAA) grafted PCL (PAA-g-PCL) as a compatibilizing agent to overcome the incompatibility in starch/PCL blended films. The authors reported a reduction in both modulus and tensile strength of the compatibilized blends with the increase of graft degree of PAA-g-PCL and such behavior, ascribing to the decrease in crystallinity of PCL matrix along with the increase in graft degree of PAA-g-PCL. Furthermore, the authors discovered that the blend containing PAA-g-PCL with 10.8% graft degree had the highest elongation at break and tensile toughness. Interestingly, the results also indicated an increase in both elongation at break and tensile toughness upon reducing graft length with the same graft degree at 11 mol%. Thus, this study demonstrated that PAA-g-PCL containing a short side chain and a high graft degree showed a better compatibilization effect in starch/PCL blends [38].

Singh et al. [70] explored the effect of PCL grafted dextran copolymer (PGD) as a compatibilizer for cornstarch/PCL blends and surface modification of granular starch via a hydrophobic coating. This study displayed an increased degradation rate compared to pure PCL since the incorporation of starch accelerates the biodegradation rate of the blend compounds. However, when surface-modified starch was replaced by high amylose corn starch or waxy maize starch, a significant reduction in the degradation rate was observed. The authors also reported an improvement in the degradation rate of compatibilized starch/PCL blend compatibilized with PGD compared to pure PCL/starch blend. From a mechanical point of view, the grafting of PCL chains at the surface of starch enhanced both rigidity and toughness with a significant increase in both Young's modulus and tensile strength from 295 to 365 MPa and 9.6 to 13.0 MPa, respectively. Moreover, it was evidenced that, whatever the compatibilizing agent, the biodegradation of starch/PCL blends starts with starch consumption and continuously increases with the content in natural filler [70].

A separate study was conducted to investigate the effect of two different compatibilizers in starch/PCL blends, namely (i) PCL grafted glycidyl methacrylate (PCL-g-GMA) and (ii) PCL-g-diethyl maleate (PCL-g-DEM). The thermo-mechanical properties of this study are enumerated in Table 2. The starch particles in compatibilized blends displayed a smoother interface with the PCL matrix than a non-compatibilized blend. The authors also displayed a higher modulus compared to that of a non-compatibilized blend incor-

porating 1 wt% of PCL-g-DEM. However, at higher DEM intakes, a significant reduction in modulus was observed, see Table 2. During the experiment, PCL-g-GMA (2 wt%) was incorporated with varying starch/PCL blends. Herein, for all the starch intakes, the tensile strength and strain at break decreased while the modulus was constant at low starch contents and significantly increased for the compatibilized blends with 30% starch. Therefore, based on the above results, it is suggested that the efficacy of PCL-g-GMA as a compatibilizer increased considerably at higher starch contents. Interestingly, PCL-g-DEM seems to provide a better compatibilization effect at a fixed starch content than PCL-g-GMA, as depicted in Table 2. Moreover, from a practical point of view, PCL-g-DEM can replace PCL-g-GMA at low starch contents [35].

**Table 2.** Comparison of thermo-mechanical properties of Starch/PCL blends [35].

Sample	Maximum Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Melting Temperature (°C)
Neat PCL	16.3	640.5	270.2	57
Starch/PCL: 10/90	15.3	489.5	321.2	57
Starch/PCL: 20/80	10.5	425.4	337.0	57
Starch/PCL: 30/70	7.1	230.0	341.8	57
Starch/PCL/PCL-g-DEM: 20/80/1	11.1	401.8	371.2	57
Starch/PCL/PCL-g-DEM: 20/80/2	10.9	384.9	342.8	57
Starch/PCL/PCL-g-DEM: 20/80/5	11.0	379.5	329.9	57
Starch/PCL/PCL-g-GMA: 20/80/1	9.2	357.2	368.3	57
Starch/PCL/PCL-g-GMA: 20/80/2	9.6	343.4	380.8	58
Starch/PCL/PCL-g-GMA: 20/80/5	11.7	431.6	372.6	57
Starch/PCL/PCL-g-GMA: 20/80/10	10.1	305.9	386.0	57
Starch/PCL/PCL-g-GMA: 10/90/2	13.6	424.6	332.0	58
Starch/PCL/PCL-g-GMA: 30/70/2	5.5	168.9	430.3	56

A separate study was carried out by Ortega-Tora et al. [32] to overcome the incompatibility between starch and PCL by synthesizing two types of compatibilizers, namely, PCL<sub>MG</sub> and PCL<sub>G</sub>. The authors reported a homogeneous dispersion of PCL particles within the polymeric matrix and an absence of voids while indicating an improved interfacial adhesion between the two polymers. Such behavior might be due to the chemical interactions between hydroxyl groups of starch and polar groups of PCL<sub>G</sub> and PCL<sub>MG</sub>. Furthermore, a significant increase in tensile strength (49%), Young's modulus (58.4%), and a drastic drop in elongation at break (84%) for pure starch/PCL blends were observed. This data confirmed the effectiveness of compatibilizing, enhancing the interfacial adhesion. However, the concentration of the compatibilizing agent in the blend did not notably affect the tensile properties. The authors also reported the variation of mechanical properties with the storage time. These results demonstrated an increase in tensile strength (15.5%), a substantial difference in ductility (65.5%), and a decrease in Young's modulus (37.1%), thus suggesting the diminishment of starch retrogradation process in these compatibilized blends. Apart from the above observations, the compatibilized blends could provide a significant reduction in both O<sub>2</sub> and CO<sub>2</sub> transmission rates compared to that of their control blends. In contrast, compatibilized blends exhibited water vapor transmission values similar to neat PCL, improving starch barrier properties. Interestingly, all the measured barrier properties were in the range required for food packaging [32].

Lopez and his coworkers fabricated starch/PCL blends compatibilized with starch grafted PCL (St-g-PCL) copolymer while using two differently processed thermoplastic starch, (i) native corn starch melt-processed with 35% *w/w* glycerol, named TPS<sub>G</sub>, and (ii)

native corn starch melt-processed with 35% *w/w* and 10% *w/w* sodium alginate, labelled as TPS<sub>GA</sub>. During the synthesis of the compatibilizers, the starch to monomer ratio was maintained at 1:0.1 and 1:10, respectively, to obtain two different compatibilizers, St-g-PCL<sub>0.1</sub> and St-g-PCL<sub>10</sub>. Smooth fracture surfaces were obtained by the blends compatibilized with 5 wt% of each compatibilizing agent. Although the addition of St-g-PCL<sub>10</sub> compatibilizer did not affect the thermal properties of the blends, the modulus and tensile strength of the blends significantly increased with the addition of St-g-PCL<sub>10</sub>. At the same time, a reduction in elongation at break was observed [39].

Apart from the above, another study was conducted to investigate the effect of starch grafted poly (L-lactide) (St-g-PLLA) as a compatibilizing agent in starch/PCL blends. The results of DSC analysis indicated a reduction of both melting temperature and crystallinity in non-compatibilized starch/PCL blends compared to that of neat PCL, and such reduction can be attributed to the addition of starch. Thus, as a filler in these blends, starch restricted PCL crystallization. Moreover, the “Molau test” (phase separation test) carried out by Chen et al. [59] indicated an improvement in interfacial compatibility between starch and PCL in the presence of St-g-PLLA. The authors also reported that the maximum values for thermo-mechanical properties were obtained by the compatibilized blend with 10% St-g-PLLA while demonstrating a decrease in all the properties when the amount of compatibilizer was increased up to 20%, indicating the unsuitability of further increments (see Table 3). On the contrary, the water contact angle measurements implied an improvement in material hydrophobicity while exhibiting an increased water contact angle in the presence of St-g-PLLA [63].

**Table 3.** The variation of thermo-mechanical properties and the degree of crystallinity of PCL in Starch/PCL blends [63].

Sample	Melting Temperature (°C)	Degree of Crystallinity of PCL (%)	Maximum Tensile Strength (MPa)	Elongation at Break (%)	Elastic Modulus (MPa)
Starch/PCL blend with 2 wt% of St-g-PLLA	59.1	47.9	13.7	125	798
Starch/PCL blend with 5 wt% of St-g-PLLA	59.3	48.5	15.2	131	813
Starch/PCL blend with 10 wt% of St-g-PLLA	60.2	49.6	16.6	139	996
Starch/PCL blend with 20 wt% of St-g-PLLA	58.7	46.3	15.1	127	862
Non-compatibilized Starch/PCL blend	57.6	41.7	8.0	516	597
Neat PCL	61.5	50.9	31.8	1109	267

### 10.2. Starch/PVA Blends

TPS and polyvinyl alcohol (PVA) blends have captured greater attention since starch lowers the cost [99], improves gas barrier properties, and enhances biodegradation. In addition, PVA can also improve the excellent mechanical, thermal, and water resistance properties of the film material [4,9,11,95,100].

Even though the combined properties of starch-PVA make them popular biodegradable blends, mechanical and water barrier properties are still lower than those of some synthetic petroleum-based polymeric materials [4,5]. However, the properties of the blends deteriorated as the starch content in the blend films increased due to poor compatibility between starch and PVA, leading to phase separation during blend preparation [11].

Moreover, the modification of starch, blend ratio, and molecular weight of PVA control the properties of these starch/PVA blends [56,58,94].

Jose and coworkers fabricated PVA/corn starch thin films via solution casting to investigate the effect of carbon nanotubes (CNT) as the compatibilizer. The authors reported a significant reduction in tensile properties with the incorporation of starch into the PVA matrix (see Table 4) compared to that of neat PVA thin film. Though some cracks were visible on the fracture surface of the blend compatibilized with 0.5 wt% of CNT, the ductility significantly increased with 2 wt% CNT, giving more compatible and homogenized blends. The study also displayed a significant increase in thermal stability with the increased addition of CNT into the blended films (see Table 4) compared to that of the control blends. Moreover, the results of SEM confirmed the variation of mechanical properties of the blends. Furthermore, the results of water absorption experiments indicate a significant reduction in water uptake from 60% to 43%, with the addition of 0.5 wt% and 2 wt% CNT, respectively [56].

**Table 4.** The summary of thermal and mechanical properties of the Starch/PVA blends compatibilized with CNT [56].

Sample	Maximum Tensile Strength (MPa)	Elastic Modulus (MPa)	Elongation at Break (%)	Residue at 500 °C (wt%)	Temperature at 90% Weight Loss (°C)
PVA	8.89 ± 0.23	61.96 ± 2.52	91.6 ± 1.5	4.48	389.8
Starch	-	-	-	11.64	560.0
Non-compatibilized Starch/PVA	6.67 ± 0.08	24.23 ± 1.86	27.5 ± 2.3	3.80	395.9
Starch/PVA blend with 0.5% of CNT	7.34 ± 0.25	66.04 ± 2.34	25.0 ± 2.0	6.27	430.5
Starch/PVA blend with 2% of CNT	8.09 ± 0.16	71.26 ± 2.22	33.7 ± 1.9	10.10	505.8

Gupta and coworkers explored the effect of both cross-linking using glutaraldehyde and fiber-reinforced starch/PVA composite blend films. As previously reported, antibacterial property plays a vital role during food packaging applications to decrease the microbial contamination in the food [101]. Compared to cross-linked films, the authors reported improved thermal and mechanical properties of 20% of *Grewia Optiva* fibre reinforced starch/PVA films. The antibacterial experiments indicated that these films had good activity against Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) bacteria. The authors also reported that the synthesized blend films might be used as potential materials in food packaging [11].

Cano et al. [14] displayed a remarkable antibacterial activity against *Listeria innocua* and *Escherichia coli* and antifungal activity against *Aspergillus niger* and *Penicillium expansum* in starch/PVA films embedding silver nanoparticles. It was also revealed that both the antifungal and antibacterial activity is highly dependent on the content of silver nanoparticles. However, the authors displayed that the incorporation of silver nanoparticles did not affect the physical properties of the films, except for their color and transparency. Furthermore, the authors also reported that the use of these developed films as food packaging applications should be restricted to fat-rich foodstuffs [14].

Widiarto examined the effect of Borax as a compatibilizing agent for sago starch/PVA blends [97]. Here, the addition of Borax to sago starch/PVA blends suggested to improve the properties of the blends through the formation of interpenetrating networks. Widiarto exhibited a significant increase in tensile strength, whereas a reduction in elongation at break with the increased incorporation of Borax. The sample obtained the maximum tensile strength of 25 MPa contained 0.6 g of Borax and 2.5 g of starch and PVA. Moreover, an increase in the weight loss of the samples with the increment of sage starch content was also observed during the soil burial test. Apart from the above observations, the results

also indicated a slight increase in the degradation rate with the incorporation of Borax. However, the effect was not significant [97].

According to the research carried out by Liu et al. [102], improved surface and mechanical properties were discovered by incorporating anthocyanins and limonene into starch/PVA blended films. Furthermore, this study demonstrated that these films effectively inhibited undesired microbial growth. In contrast, the tests on pasteurized milk showed that the films could prevent milk spoilage, simultaneously indicating the acidification of milk [102].

Hiremani and coworkers prepared 7-hydroxy-4-methyl coumarin (7H4MC) doped PVA/oxidized maize starch blend films using solution casting. The authors showed enhanced mechanical properties due to changes in the structure of the blend films. The authors also reported that the blend films containing 0.004 and 0.006 g of 7H4MC exhibited increased tensile strength and percentage elongation at break compared to that of the control blend film, and such behavior ascribed to hydrogen bonding interactions between the components of the blend. Moreover, the results obtained from the food compatibility test revealed that the migration rates of all the blend films were below the overall migration limit of 60 mg/kg [103].

### 10.3. Starch/PBS Blends

Currently, it has become a common practice to incorporate starch in the PBS matrix to achieve a cost reduction, improved rate of biodegradation, and sustainable film materials with numerous properties, while expanding its applications in packaging and flushable hygiene products remains possible [31,67]. However, the blending mechanism of thermo-plastic starch and PBS is quite difficult due to their immiscibility caused by differences in their viscosity and interfacial tension [67].

Yin and coworkers fabricated biodegradable TPS/PBS blends using maleic anhydride grafted PBS (MA-g-PBS or rPBS) as an interfacial compatibilizing agent. The authors reported that, although compatibilized, the effect of compatibilization on the mechanical properties of TPS-rich blends was not significant, though the amount of added compatibilizer was increased. This was in agreement with the report of Ren et al. [89], and such behavior might be due to an insufficient amount of compatibilizer to form effective chemical bonds between starch and PBS. Despite the fact that maximum tensile strength and the elongation at break for PBS/TPS (60/40) blend were 6.4 MPa and 4%, respectively, with the incorporation of the compatibilizer, the elongation at break could reach ~20%, while the tensile strength of the blend increased over two-fold. The authors also reported a better adhesion and evenly dispersed starch particles at higher contents of the compatibilizing agent. The observations related to water absorption experiments revealed that incorporating hydrophobic PBS lowered the water absorption of TPS and reduced the water sensitivity of TPS/PBS blends. However, the amount of compatibilizer did not affect the water resistance of TPS/PBS blends. The authors suggested that the compatibilized TPS/PBS blends with rPBS, combined with biodegradability, high strength, and water resistance, could represent a strong candidate as packaging materials [24].

Another study was carried out to investigate the effect of starch grafted PBS as a compatibilizer on the properties of starch/PBS blends. To evaluate the performance of compatibility of starch/PBS blends, the phase separation in terms of the gap between starch and PBS was examined. The results indicated that the compatibilized blends had few gaps between the starch granules and PBS. Moreover, the starch-g-PBS could provide better compatibility in the blends containing 20% and 40% starch. Suchao-M et al. [37] also reported an improvement in the modulus and higher yield strengths in compatibilized blends, and this behavior might be due to the fact that the compatibilizer provides the interfacial adhesion between starch and PBS, resulting in an improvement of the stress transfer between the two-component phases. Apart from the above-described properties, melt viscosity plays a significant role as a guideline for processing. According to the results obtained related to melt viscosity index, the melt viscosity index of the compatibilized

blends containing 20% and 40% starch was ~5–7 g/10 min, which is suitable for the production of foam products [37].

Besides, Fahrngruber et al. [67] prepared TPS/PBS blends in the presence of two different types of compatibilizer systems based on native starch and pre-plasticized/destructurized starch. The study demonstrated an improvement in elongation at break, maximum tensile strength, and tear resistance in the compatibilized blends with increased starch and pre-plasticized/destructurized starch contents in the compatibilizers. However, with the addition of a native starch-based compatibilizer, only limited stability was provided. In contrast, the destructurized starch-based compatibilizing agent could provide a larger interaction surface (amylose/amylopectin-PBS, and probably also glycerol-PBS) and give a more homogenized sample. Apart from the above observations, the water vapor permeability increased in all the compatibilized samples compared to that of the pure TPS/PBS blend, and such behavior might be due to the improved incorporation of native starch and TPS within the polyester matrix, due to which the hydrophilic characteristics of the starch component became more dominant. Furthermore, the disintegration results imply that, after 10 days, visible cracks developed on the surfaces of both compatibilized and non-compatibilized samples, transforming into holes after 20 days. However, the disintegration of the pure TPS/PBS blend sample processed slightly faster compared to that of the compatibilized samples [67].

#### 10.4. Starch/PLA Blends

Although PLA has suitable properties related to packaging applications, the usage has been reduced due to high cost, brittleness, poor processability window, high moisture permeability, and low toughness [77,78,104]. Therefore, the low price and completely biodegradable nature of starch make it possible to be used as filler in PLA, improving the properties suitable for various applications [78,105].

Huneault and Li [33] synthesized PLA grafted maleic anhydride (PLA-g-MA) to eliminate the incompatibility between both starch and PLA in TPS/PLA blends. The authors reported that, in non-compatibilized blends, the morphology was coarse when the TPS particle size ranged from 5 to 30  $\mu\text{m}$ , whereas for the compatibilized blends, the TPS particles were nearly spherical and relatively homogeneous when the average diameters of the particles ranged from 2.2 to 4.2  $\mu\text{m}$ . Therefore, MA-g-PLA significantly decreased the TPS phase size, implying that interfacial reactions decrease the blends' interfacial tension. Apart from the above observations, the tensile modulus decreased progressively with the increased addition of TPS in the blends. The results also revealed that the modulus was nearly unaffected by compatibilization. Though the authors also displayed a slight increase in maximum tensile strength, the dominant effect in the entire system was the reduction of tensile strength with the increment of TPS content in the blends. Moreover, for non-compatibilized blends, the elongation at break occurred in the range of 10–20%, which was slightly higher than for pure PLA, whereas for compatibilized blends, a long plastic deformation plateau leading to elongation at break over 150% was recorded. This behavior might be due to the coarse blend dispersion leading to premature failure since the larger dispersed particles may act as defects that resulted in the formation of cracks in the material [33].

Akrami et al. [92] explored the effect of maleic anhydride grafted poly-ethylene glycol grafted starch (mPEG-g-St) as a compatibilizer for biodegradable TPS/PLA blend composites. This study demonstrated that, in compatibilized blends, spherical particles were formed, and a better dispersion was obtained. This is probably due to improved interfacial adhesion between the two polymer phases in the blends compared to that of control blends. The authors also displayed a significant increase in tensile strength with the increased incorporation of mPEG-g-St, see Table 5. However, the values obtained for elongation at break were small while the samples cracked up to 1.49% for the best case, and such behavior can be attributed to the brittleness of both PLA and starch. Furthermore, the authors also displayed no significant effect on the rate of degradation by the compatibilizer.

This behavior is due to the constant concentration of the TPS in all the samples, which plays a vital role in the initiation and development of degradation [92].

**Table 5.** Thermo-mechanical properties and the variation of the degree of crystallinity of the blends [92].

Sample	Melting Temperature (°C)	Degree of Crystallinity of PLA (%)	Maximum Tensile Strength (MPa)	Elastic Modulus (MPa)	Elongation at Break (%)
Pure PLA	169.8	48.56	55 ± 2	2500 ± 50	-
Pure TPS/PLA blend	166.4	54.70	18 ± 1	1701 ± 87	1.34 ± 0.06
TPS/PLA blend with 5 phr of mPEG-g-St	165.3	54.56	19 ± 2	1815 ± 106	1.42 ± 0.10
TPS/PLA blend with 10 phr of mPEG-g-St	165.3	52.70	21 ± 3	1631 ± 74	1.49 ± 0.21
TPS/PLA blend with 15 phr of mPEG-g-St	166.2	49.01	18 ± 1	1563 ± 45	1.42 ± 0.14
TPS/PLA blend with 10 PEG	164.7	47.32	14 ± 2	1595 ± 77	1.15 ± 0.13

Another study was carried out to investigate the effect of three different compatibilizing strategies in TPS/PLA blends. Two different strategies were based on the formation of urethane linkages, peroxide coupling, and the addition of PLA grafted amylose (PLA-g-amylose). The results of this study exhibited better thermal and mechanical properties with the addition of 2 wt% benzoyl peroxide (BP) as the compatibilizer. The reason for improved thermal and mechanical properties in blends with BP include that, after heating, peroxide decomposes into radical species, which react either with amylose or with PLA chains. When considering the compatibilization effect of blends containing di-isocyanate (MDI), the addition of 2 wt% MDI into the blends caused an increase in PLA crystallinity and the modulus of these blends, and this behavior is in agreement with the change of crystallinity. However, the mechanical properties improved dramatically in all the compatibilized blends while exhibiting the highest values for maximum tensile strength (40.5 MPa) and elongation at break (3.5%) by the blend possessing the highest amount of compatibilizer and the lowest amount of dried starch. Interestingly, with the addition of 1 wt% PLA-g-amylose as a compatibilizer into the blends, an evolution of thermal and mechanical properties was observed, demonstrating a remarkable increase in tensile strength without decreasing the elongation at break [106].

Wang et al. examined the effect of low toxicity maleic anhydride as a compatibilizer in dried thermoplastic corn starch (DTPS)/PLA blends. Here, dicumyl peroxide (DCP) was used as the initiator along with MA. The authors reported a better dispersion between TPS and PLA while the granule size of starch decreased dramatically in the presence of MA and DCP compared to that of control blends. Moreover, it was observed that, with the increment of the starch contents in the blends, the mechanical properties worsened notably, and such behavior could be attributed to the poor interfacial adhesion between the two phases. However, in all the compatibilized blends, the mechanical properties improved dramatically while exhibiting the highest values for maximum tensile strength (40.5 MPa) and elongation at break (3.5%) by the blend possessing the highest amount of compatibilizer and the lowest amount of dried starch. Interestingly, even at increased starch contents in the blends, the mechanical properties did not worsen considerably in the presence of MA along with DCP [90].

Liu and his coworkers synthesized PLA grafted glycidyl methacrylate (GPLA-x) as the compatibilizing agent to improve the compatibility in PLA/TPS blended sheets. The authors reported an enhanced dispersion of the starch granules in the PLA matrix while reinforcing interface bonding between PLA and starch with the addition of GPLA-x. The expected reaction mechanism of GPLA-x compatibilizer might be that GPLA consists of

the glycidyl functional group of the epoxide, which may react with OH groups of glucose units in starch. The study also provided a remarkable increase in maximum tensile strength from 18.6 to 29.3 MPa, tensile modulus from 510 to 901 MPa, and elongation at break from 1.8% to 3.4% for the non-compatible blend and PLA/TPS/GPLA-11 blend, respectively (see Table 6). Moreover, the medium resistance test implied well improved stability by compatibilized blends against all the three mediums: 0.5 M HCl, 0.5 M NaOH, and H<sub>2</sub>O solutions, demonstrating the best stability by PLA/TPS/GPLA-11 sample. In addition, the blends did not become swollen or sticky when contacted with water. Overall, the authors suggested the potential use of these blends to produce packaging materials, disposable goods, electronic materials, structures, and tissue engineering materials [91].

**Table 6.** Summary of the comparison of properties of Starch/PLA (50/50) blends compatibilized with GPLA [91].

Sample	TS (MPa)	E (MPa)	$\varepsilon$ (%)	$T_g$ (°C)	$T_m$ (°C)	Weight Change		
						0.5 HCl	0.5 NaOH	H <sub>2</sub> O
Pure PLA	51.4 ± 7.2	2350 ± 150	4.3 ± 0.5	-	-	-	-	-
Starch/PLA blend	18.6 ± 3.8	510 ± 62	1.8 ± 0.4	56.3	146.7	+18.2	-35.2	+18.2
Starch/PLA blend compatibilized with GPLA-1.8	27.2 ± 4.2	730 ± 71	3.1 ± 0.5	54.8	143.8	+5.3	-18.2	+5.3
Starch/PLA blend compatibilized with GPLA-5.1	28.3 ± 5.7	750 ± 69	3.2 ± 0.5	54.4	143.2	+4.2	-16.2	+4.2
Starch/PLA blend compatibilized with GPLA-8.6	28.4 ± 5.4	850 ± 80	3.2 ± 0.4	54.1	143.1	+2.4	-16.3	+2.4
Starch/PLA blend compatibilized with GPLA-11	29.3 ± 5.8	901 ± 62	3.4 ± 0.5	54.1	143.1	+1.8	-15.1	+1.8

Note: TS; Maximum tensile strength, E; Elastic modulus,  $\varepsilon$ ; Elongation at break,  $T_g$ ; Glass transition temperature,  $T_m$ ; Melting temperature.

Wootthikanokkhan and coworkers investigated the effect of polylactic acid grafted maleated thermoplastic starch (PLA-g-MTPS) as a compatibilizer in PLA/TPS blends. This study revealed that the tensile properties of the blends were highly dependent on the type of copolymer used. As the PLA grafted maleic anhydride (PLA-g-MA) was added into the blends, a slight decrease in the tensile properties compared to that of control blends was observed. However, with the incorporation of PLA-g-MTPS into PLA/TPS 80/20, the blend could display a notable increase in tensile strength compared to that of the control blends, while the compatibilizing efficacy of the PLA-g-MTPS copolymer became more pronounced when the starch content was further increased to 30% and 40%. A similar behavior could be observed for both elongation at break and toughness [98].

Clasen et al. studied the effect of maleic anhydride as a compatibilizer in PLA/TPS blends. Here, three types of blends were prepared to evaluate the effect of MA as a compatibilizer, namely: (i) TPS/PLA (70/30) blend named as 'B0', (ii) TPS/PLA (70/30) blend, which was compatibilized using PLA-g-MA, labelled as 'B1', and was prepared by grafting 2% of MA onto PLA, (iii) starch/PLA/glycerol/MA/dicumyl peroxide (49/29.2/21/0.6/0.2) blend named as 'B2'. This observed that sample B0, which did not contain MA demonstrated a greater rigidity and a lower strain than the blends that contained MA as the compatibilizer. However, Young's modulus of samples B1 and B2 was lower than sample B0, see Table 7. The authors also reported a reduction of the crystallinity of PLA with the incorporation of MA into the blends (see Table 7). Though a reduction in water vapor permeability and an increase in gas barrier properties for both samples B1 and B2 compared to sample B0 was highly expected, the incorporation of MA into the samples did not affect the gas barrier properties and the water adsorption. The authors also reported that MA

was capable of acting as a compatibilizer in TPS/PLA blends and as a plasticizer, reducing the glass transition temperature of the samples [107].

**Table 7.** The variation of crystallinity of PLA, Young's modulus and the water vapor permeability in Starch/PLA blend films [107].

Blend	Degree of Crystallinity of PLA (%)	Young's Modulus (MPa)	WVP $\times 10^{-6}$ (mgh <sup>-1</sup> Pa <sup>-1</sup> m <sup>-2</sup> )
B0	52	143 $\pm$ 15	0.67 $\pm$ 0.12
B1	41	26 $\pm$ 6	1.04 $\pm$ 0.04
B2	38	11 $\pm$ 2	1.12 $\pm$ 0.31
Neat PLA	54	-	-

The effectiveness of PCL after grafting with maleic anhydride and glycidyl methacrylate in corn starch/PLA blends was also investigated [93]. Here two modification reactions were carried out to prepare two different types of PCL-based compatibilizers: (i) Modification of MA and glycidyl methacrylate to obtain PCL<sub>MG</sub>; (ii) Modification with only using glycidyl methacrylate to obtain PCL<sub>G</sub>. The authors discovered that the blend containing 20% of PLA compatibilized with 5% PCL<sub>G</sub> exhibited the most homogeneous structure with the highest dispersion level of PLA in the starch matrix. According to thermo-gravimetry analysis (TGA) results, all the compatibilized and non-compatibilized blends exhibited three degradation phases at different intensities depending on the composition of the mixture. However, both the initial degradation temperature and the temperature at the maximum degradation rate of polymers were closer to the corresponding temperature of starch due to its higher ratios in the blended sheets. Moreover, in compatibilized blends containing 20% PLA, there was a significant increase in elastic modulus (a nearly two-fold increase with PCL<sub>2.5MG</sub>) and tensile strength (a nearly 1.5-fold increase with the incorporation of PCL<sub>2.5G</sub>) when compared to the control blend. Even though the partial substitution of PLA into starch reduced the water vapor permeability of the blends, there was no significant reduction in oxygen gas permeability. Interestingly, the reduction in water vapor permeability in the compatibilized blend with 40% PLA and 5% PCL<sub>G</sub> was more remarkable. Furthermore, it was reported that, from a mechanical point of view, the blend containing 20% PLA and 5% PCL showed comparatively better tensile strength and extensibility. Besides, dry or partially dehydrated products and fatty or oxidation-sensitive foods could be adequately packaged with these films, thus improving their preservation [93].

#### 10.5. Starch/PHBV Blends

To overcome the drawbacks of PHBV, efforts have been made towards PHBV/thermoplastic starch (TPS) blends to reduce the cost and improve the biodegradation rate of PHBV [80,81]. However, only a limited number of research has been conducted to explore the effect of compatibilization of starch/PHBV blends.

Magalhaes et al. [80] prepared PHBV/TPS blends compatibilized by organically modified montmorillonite to investigate the mechanical and surface properties. The authors reported that the interfacial adhesion between PHBV and TPS increased and the sizes of particles were also significantly reduced with the increased incorporation of the compatibilizer amount. According to the results obtained through XRD patterns, a decrease in the crystallinity fractions in both phases was observed for all the compatibilized blends. Interestingly, the addition of less hydrophilic PHBV and organically modified montmorillonite into the starch matrix could reduce the humidity adsorption of each blend. When considering the effect of compatibilization on mechanical properties, both the tensile strength at break and Young's modulus gradually increased with increasing compatibilizer amount while decreasing elongation at break than the non-compatibilized PHBV/TPS blend. The maximum values for the tensile strength at break (13 MPa) and Young's modulus (800 MPa) were obtained for the blend compatibilized with 10% organically modified montmoril-

lonite. The authors also reported an increase in weight within the first two weeks for all the compatibilized and non-compatibilized films due to water adsorption by the films due to their hydrophilic nature during the biodegradation test. However, after 150 days, TPS in the non-compatibilized blend was completely degraded. Moreover, the biodegradation rate drastically increased from 76% to 90% with organically modified montmorillonite. Moreover, all PHBV/TPS blends degraded faster than PHBV alone. Therefore, it was evidenced that organically modified montmorillonite acted as a compatibilizing agent for the two immiscible polymer pairs, namely PHBV and thermoplastic starch [80].

#### 10.6. Starch/PBAT Blends

Fourati et al. [68] prepared TPS/PBAT blended sheets to investigate the compatibilization effect of maleic anhydride (MA), citric acid (CA), and PBAT grafted MA (PBAT-g-MA) as compatibilizing agents. According to the results, the strain at break of neat TPS was initially low (7%) and increased to 185% after blending with PBAT without adding any of the compatibilizers. However, when compatibilized with 2% of MA and 2% of CA added, the strain at break decreased to a level between 12% and 30%, and the evolution did not change notably with the increased addition of MA or CA up to 6%. Although the tensile strength at break decreased in the presence of both MA and CA to around 8 MPa, the best mechanical properties were achieved when the blend was compatibilized with 2% PBAT-g-MA with a maximum tensile strength of 12 MPa, elongation at break of 380%, and a modulus of 58 MPa. Moreover, the minimum amount of water was absorbed in the presence of PBAT-g-MA. The authors also reported an enhanced interfacial adhesion in the presence of PBAT-g-MA occurred via ester-linkage between the grafted MA onto starch and PBAT. Based on the above facts, the authors reported PBAT-g-MA as the best compatibilizer for TPS/PBAT 60/40 blends over MA and CA compatibilizers alone [68].

Ren and coworkers explored the effect of maleic anhydride as a compatibilizer for TPS/PLA/PBAT blends prepared via one-step melt processing. The results of the study indicated an increase in both tensile strength and elongation at break for the whole composition range after incorporating a small amount of compatibilizer into the blends. However, as PBAT content was increased, the elongation at break increased. This behavior could be observed for both compatibilized and non-compatibilized blends. Moreover, it was deduced from SEM images that, in non-compatibilized blends, large starch phase domains could be found, while after compatibilized, the starch granules were mostly melted and formed a continuous phase with synthetic polymer matrix. Therefore, the non-compatibilized blends showed lower mechanical properties compared to those of compatibilized blends. The above results imply that the anhydride functionalized polymer acted as a hydrophobic coating around hydrophilic TPS, thus improving the interfacial adhesion between the blend components (see Figure 6), thereby producing finer and uniform morphology with improved mechanical properties. In addition, the authors demonstrated an increase in melt flow index of the compatibilized blends, suggesting the suitability of the prepared blends for injection moulding. Furthermore, it was also reported that the equilibrium water content increased from 16% to 20% as the PBAT content was increased from 0% to 50%. However, the equilibrium water uptake of the compatibilized blends was comparatively lower than the non-compatibilized blends [89].

Olivato et al. [108] fabricated corn starch/PBAT blown films by incorporating CA and MA compatibilizing agents. The blends were prepared according to the compositions depicted in Table 8 while maintaining the starch: BAT weight ratio at a constant value at 55:45. Though the authors reported that higher concentrations of MA in the films could produce more opaque films, the effect of CA was the most significant factor (see Table 8). Such observations could be attributed to the cross-linking reactions that occurred during the compatibilization. Cross-linking increases the polymeric chain compaction, making it more difficult for light to pass through the matrix, resulting in more opaque films. As reported by the authors, CA positive affected the maximum tensile strength of the blended films while producing stronger films (see Table 8). Olivato and coworkers also revealed

that both CA and MA allowed the formulations to overcome the deficiencies associated with the incompatibility between TPS and PBAT during the blend preparation. Besides, though MA is a more reactive compound in similar concentrations, the efficacy of MA as a cross-linking agent was lower when compared with CA. The comparison of water vapor permeability, opacity, and mechanical properties of the samples is enumerated in Table 8 [108].

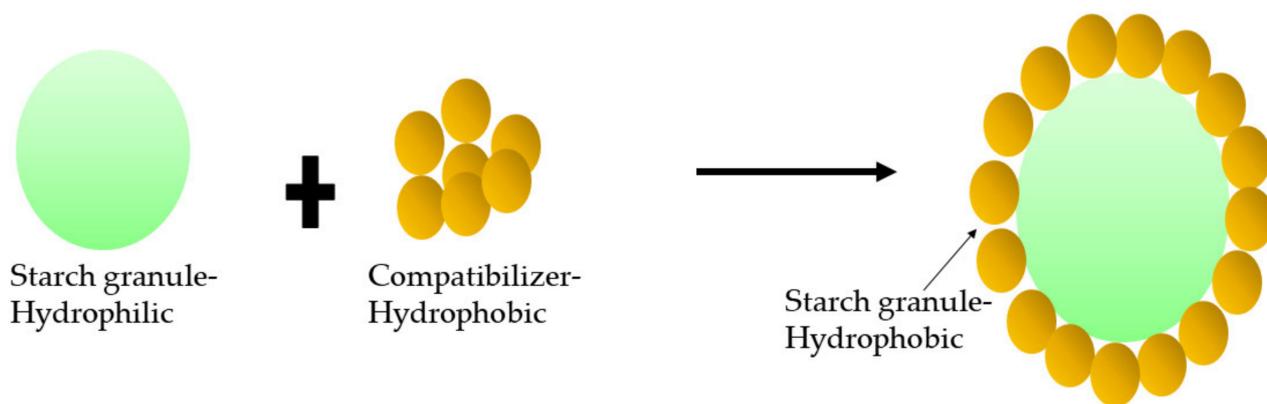


Figure 6. The formation of hydrophobic starch granule.

Table 8. Summary of the study [108].

Sample	Sample Composition (wt%)			WVP $\times 10^{-10}$ ( $\text{gs}^{-1}\text{m}^{-1}\text{Pa}^{-1}$ )	Opacity ( $\%\mu\text{m}^{-1}$ )	TS (MPa)	$\epsilon$ (%)
	Glycerol	CA	MA				
1	10.0	0	0	$3.600 \pm 0.026$	$0.452 \pm 0.006$	$4.320 \pm 0.317$	$264.466 \pm 21.332$
2	8.5	1.5	0	$1.966 \pm 0.017$	$0.656 \pm 0.006$	$6.575 \pm 0.115$	$16.386 \pm 1.259$
3	8.5	0	1.5	$3.847 \pm 0.815$	$0.203 \pm 0.005$	$5.512 \pm 0.487$	$10.306 \pm 2.293$
4	9.25	0.75	0	$1.789 \pm 0.03$	$0.419 \pm 0.009$	$5.592 \pm 0.109$	$383.351 \pm 11.218$
5	9.25	0	0.75	$3.548 \pm 0.207$	$0.301 \pm 0.003$	$5.268 \pm 0.339$	$13.868 \pm 2.737$
6	8.5	0.75	0.75	$4.650 \pm 0.355$	$0.256 \pm 0.012$	$5.559 \pm 0.522$	$17.549 \pm 2.494$
7	9.0	0.5	0.5	$2.147 \pm 0.136$	$0.363 \pm 0.006$	$6.534 \pm 0.384$	$5.855 \pm 0.604$
8	9.0	0.5	0.5	$2.011 \pm 0.227$	$0.381 \pm 0.008$	$6.054 \pm 0.774$	$6.093 \pm 0.525$

Note: TS; Maximum tensile strength,  $\epsilon$ ; Elongation at break.

A study was conducted to examine the effect of citric acid (CA) as a compatibilizer in starch/PBAT blends due to its multicarboxylic structure [109]. CA can also act as a plasticizer, cross-linking agent, and hydrolytic agent. It was observed that when the concentration of CA in the blend films was increased from 0.5% to 2.5%, the amount of donuts in the blend decreased, implying the fragmentation of the starch granules during the processing. This could be due to the friction and temperature caused during the extrusion process and the specific action of CA acting as a hydrolytic agent at the chains. Besides, the authors also reported a reduction in maximum tensile strength when the concentration of CA in the blends was increased. Such behavior implies that citric acid acted not only as a cross-linking agent but also as a plasticizer. Interestingly, the water vapor permeability reduced with the increased addition of citric acid into the blends as a compatibilizer since introducing new ester groups in the starch chain causes increasing hydrophobicity. Moreover, the authors also reported that the amount of incorporated CA as a compatibilizing agent should be adjusted and optimized to the required application [109].

### 10.7. Starch/PHB Blends

Blending PHB with thermoplastic starch (TPS) has become one of the widely used methods to address the previously mentioned drawbacks of PHB alone while reducing the cost and maintaining biocompatibility and renewability. However, the necessity of improving the compatibility between PHB and TPS has drawn particular attention due to the immiscibility between these two separate components [22,110].

An investigation has been carried out by Ma et al. [22] to explore the effect of in situ compatibilization via maleic anhydride (MA) and benzoyl peroxide (BPO) in PHB/polyethylene-co-vinyl acetate (EVA)/starch blends. According to the results obtained through SEM images, in a non-compatibilized PHB/EVA/starch blend, large starch particles were observed in the PHB matrix while EVA existed as fine domains. However, with the incorporation of MA into the blends, the size of starch particles reduced, suggesting a better adhesion between the phases, while starch migrated from the PHB matrix into the EVA phase when the MA content was increased to 0.18 and 0.36 wt%. The authors also reported a significant variation in the mechanical properties of the blends. Although the maximum tensile strength at break first increased with the addition of MA content and then gradually decreased, the elongation at break increased monotonically with the increment of MA content in the blends. Therefore, the resultant values for lower tensile strength and higher elongation at break of the blends were obtained at high MA contents, whereas the highest tensile strength was obtained for the blend containing 0.09 wt% of MA valuing ~16.5 MPa, see Table 9. Besides, the tensile tester recorded the work of each PHB/EVA/TPS specimen automatically, and the results indicated that the work increased with the MA content, pronouncing that toughness increased by in situ compatibilization [22].

Tables 9 and 10 summarize the thermal properties, mechanical properties, water absorptivity, degradation rate, oxygen permeability, water vapor permeability, water vapor transmittance rate, gas transmittance rates, and opacity values of the compatibilized blends reported previously.



Table 9. Cont.

Formulation of the Best Performance	TS (MPa)	$\epsilon$ (%)	E (MPa)	Tensile Toughness (MPa)	Water Absorption (%)	Tear Resistance (MPa)	Melt Flow Index (g/10 min)	Biodegradation	Ref.
0.05 g of oxidized maize starch, 2 g of PVA and 0.006 g of 7-Hydroxy-4-methyl coumarin	22.8 $\pm$ 2	147.1 $\pm$ 2.6	177.8 $\pm$ 3.1	-	44.3 $\pm$ 1.1	-	-	-	[103]
Starch/PCL (40/60) blend with Polyacrylicacid-g-PCL at 10 phr with a 11 mol% grafting degree	15	35	530	1.5	-	-	-	-	[38]
PCL/Starch (70/30) blend with surface treated starch granules	17.1	528	216	-	-	-	-	250 days	[70]
TPS/PCL (90/10) blend with Starch-g-PCL consisting of starch: monomer ratio of 1:10	63 $\pm$ 6	17.1 $\pm$ 0.5	88.2 $\pm$ 5.8	-	-	-	-	-	[39]
TPS/PBAT (60/40) blend with 2 wt% PBAT-g-MA	12	380	58	-	-	-	-	-	[68]
TPS/PLA (50/50) blend with 1 wt% MA	28	2.5	1650	-	12	-	-	-	[89]
Corn starch: PVA at 1:1 <i>w/w</i> with 40% nano-sized poly (methyl methacrylate-co-acrylamide) particles	86.7	6.5	-	-	-	-	-	-	[2]
TPS/PLA (27/73) blend with PLA-g-MA	45	250	2600	-	-	-	-	-	[33]
Cassava starch: PVA (1:4) with 3 wt% SiO <sub>2</sub> particles	7	650	-	-	8	-	-	-	[114]
TPS/PLA (60/40) blend with 1 wt% Amylose-g-PLA	6.5	2.5	360	-	-	-	-	-	[106]
PLA/Starch/Glycerol/MA/DCP (50/35.4/14.3/0.5/0.05)	40.5	3.5	-	-	-	-	-	-	[90]
PLA/TPS (80/20) blend with 5 wt% of PLA-g-Maleated TPS	4	-	550	-	-	-	22.3 $\pm$ 1.7	-	[98]

Note: TS; Maximum tensile strength, E; Elastic modulus,  $\epsilon$ ; Elongation at break.

**Table 10.** Comparison of properties of compatibilized Starch/Synthetic biodegradable polymer blends ctd.

Formulation of the Best Performance	TS (MPa)	$\epsilon$ (%)	E (MPa)	T <sub>m</sub> (°C)	Gas Transmittance Rate (m <sup>3</sup> /m <sup>2</sup> .Day.Bar)	OP ( $\times 10^{14}$ cm <sup>3</sup> .m <sup>-1</sup> .s <sup>-1</sup> . Pa <sup>-1</sup> )	WVT (m <sup>3</sup> /m <sup>2</sup> .Day.Bar)	Biodegradation	Opacity (% $\mu$ m <sup>-1</sup> )	WVP ( $\times 10^{-10}$ gs <sup>-1</sup> m <sup>-1</sup> Pa <sup>-1</sup> )	Ref.
Starch/Glycerol/PCL/PCL-g-glycidyl methacrylate (64.1/19.23/12.82/3.85)	5.3 ± 0.6	36 ± 3	315 ± 32	57.1 ± 0.5	O <sub>2</sub> : 1.84 ± 0.03 CO <sub>2</sub> : 96 ± 9	-	5.7 ± 0.3	-	-	-	[32]
Potato starch: PVA at 3:5 v/v with STMP, boric acid and limonene 0.1 mg each	4.51	11.39	-	-	-	-	-	-	-	-	[51]
Starch/PCL (50/50) with 10 wt% Starch-g-poly(L-lactide)	16.6	139	996	60.2	-	-	-	-	-	-	[63]
Pea starch: PVA: Glycerol: AgNO <sub>3</sub> (1:0.5:0.25:0.16) weight basis	30.7	33.4	771 ± 42	-	-	-	-	-	-	3.8 ± 0.2	[14]
Starch/PBAT (55/45) blend with 8.5 wt% glycerol and 1.5 wt% Citric acid	6.57 ± 0.12	16.386 ± 1.259	-	-	-	-	-	-	0.656 ± 0.006	1.966 ± 0.017	[108]
Maize starch: PVA: TiO <sub>2</sub> (1:1:0.05)	31.3	89.1	230.39 ± 6.39	200.2	-	-	-	-	-	6.48 ± 0.78	[115]
TPS/PLA (70/30) blend with 10 phr of maleic anhydride grafted poly-ethylene glycol grafted starch	21 ± 3	1.49 ± 0.21	1631 ± 74	165.28	-	-	-	40% increment than for pure PLA	-	-	[92]
TPS/PLA (50/50) blend with 15 wt% PLA-g-glycidyl methacrylate with a grafting degree of 11 mol%	29.3 ± 5.8	3.4 ± 0.6	901 ± 62	143.05	-	-	-	-	-	-	[91]
TPS/PLA (80/20) blend with 5 wt% PCL-g-glycidyl methacrylate	8.1 ± 0.8	12.9 ± 1.5	101 ± 15	-	-	22.1 ± 1.9	-	-	-	5.1 ± 0.2	[93]

## 11. Starch/Synthetic Biodegradable Polymer Blends for Packaging Applications

Compared to current global plastic production, it has been predicted that plastic packaging will increase by 2–3-fold in 2030 and 2050, respectively. Moreover, around 26% of the overall plastic production has been used for packaging applications [116]. Therefore, replacing the inert petroleum-based plastic materials with “green plastics” has been a timely matter. However, biodegradable polymers are restricted for some applications due to their relatively high production cost, comparatively lower mechanical and thermo-mechanical properties, and water sensitivity compared to certain non-degradable commodity polymers. Thus, numerous biodegradable polymer blends have been developed to overcome these limitations. Currently, Europe is leading the movement in advancing biodegradable polymer blends for packaging across the globe [117].

Although most carbohydrate polymers are widely utilized as food, the use of carbohydrates in other applications has gained significant attraction over the last few years. This could be ascribed to the wide availability and renewable nature of many carbohydrates, including starch. Interestingly, according to the European Bioplastics market, starch-based blends have captured 18.7%, thus increasing the market for bioplastics. In contrast, starch-based blends have found applications in short lifespan service and flexible and rigid packaging applications owing to their attractive properties, such as biodegradability and gas barrier properties.

Some of the prominent applications of starch composites and blends that exist in the current market are as follows:

- (i) Loose fill packaging: For the production of loose-fill packages using starch-based products, corn, wheat, hydroxypropylated high amylose corn starch containing a small number of additives, including PVA, glycerol, polyethylene glycol (PEG), or silicon dioxide, and methyl-acrylate grafted corn starch is used (see Table 11) [118].
- (ii) Starch-polyester films: Starch/PCL film composites and blends are currently used in the market as compost bags (see Table 11) [118].

**Table 11.** Commercially available starch-based blends available for packaging applications.

Blend	Supplier	Brand Name
Starch/Aliphatic polyesters	Showa Denko	Bionolle/Starcle
Starch/Aliphatic aromatic polyesters	Limagrain	Biolice
Starch/PCL	Novamont	Mater-Bi
Methyl acrylate grafted corn starch-based blend	Uni-Star Industries	Star-Kore
Starch/Co-polyester	Teknor Apex	Terraloy
Starch/Aliphatic aromatic polyester	Novamont	Mater-Bi
Starch/PCL	Michign State University	Envar
Starch/Aliphatic aromatic polyester	Compostables	Cereplast
Starch/Aliphatic polyesters	Biograde	Biograde

Some of the commercially available starch-based blends for packaging applications are depicted in Table 11.

## 12. Challenges and Future Perspectives for the Development of Starch/Synthetic Biodegradable Polymer Blends for Packaging Applications

Due to the increasing market of starch blends as rigid and flexible packaging materials, it is vital synthesizing biodegradable materials with optimum performances comparable to those of conventional inert plastics. From a cost and practicality point of view, it is preferable that the starch-based blends contain a high percentage of starch. However,

remarkable and faster growth might be expected for the products synthesized using 100% biodegradable polymers, including PLA and PVA, due to significant hurdles existing during the incorporation of high amounts of starch (>25–30 wt%) without compromising material properties.

Although a smaller amount of compatibilizing agent is sufficient to obtain better mechanical properties, surface properties, and thermal properties, the performance of the non-biodegradable polymers is still better than those of starch-based blends. Despite the advantages of biodegradable polymers, mechanical performance is a significant factor determining the materials' ability to process and manufacture at a large scale and apply in different packaging fields. The barrier performances also play a vital role in maintaining the shelf-life of the packaged products. However, starch can be considered efficient in gas barrier properties but not effective in water barrier properties. Interestingly, in some cases, the compatibilized starch/synthetic biodegradable polymer blends exhibited superior mechanical and oxygen barrier performances compared to conventional inert plastic materials.

A wide range of physical, chemical, and other modification techniques can be applied to improve the properties of the starch blends. For instance, the esterification of starch with fatty acids seems to be a significant modification that improves the hydrophobicity and thermo-plasticity, thus increasing the usefulness of this polysaccharide in packaging production. Moreover, the water barrier properties of starch-based blends need to be improved to compete with conventional plastic. Usually, the porosity of a certain material reflects its ability to uptake moisture. Hence, the porosity of the starch-based blends should be estimated prior to their applications [119–121]. Furthermore, antimicrobial activity, sealing properties and food spoilage ability are imperative for food packaging materials. Therefore, those properties of starch/polymer blend before using as food packaging materials.

The source of starch used for blending also plays a significant role. For example, Morgan and Choct [122] reported that cassava starch is more suitable to produce TPS owing to its remarkable properties, such as higher clarity, low glass transition temperature, and good gel stability [122]. According to Gunawardene et al., the gelatinization temperature of extracted cassava starch was reported to be 43.27 °C, that is comparatively lower than other starch types [123].

Over the past few years, cassava cultivation has been drastically increased due to its easy-growing nature at the expense of minimum labor and fertilization, higher yield, and comparatively higher stability against diseases and pests. The authors also reported that cassava cultivation is abundant in many countries due to its ability to grow in any soil. Most importantly, the cassava harvesting area and production have increased by 91.7% and 67.82%, respectively, during the past 30 years, and this is a considerable improvement when compared with other food crops, such as maize, rice, wheat, millet, potato, barley, oats, and sweet potatoes [124]. Therefore, for further improvement in the cassava value chain, the productivity and yield of cassava should be increased.

Undoubtedly, the research on the compatibilization of starch/synthetic biodegradable polymer blends will continue to rise in the near future. Future research should focus on starch-based blends that possess better water barrier properties, antibacterial properties, and sealing properties containing starch or modified starch for industrial-scale packaging applications.

### 13. Conclusions

This review presents the developments in the compatibilization techniques available for starch/synthetic biodegradable polymer blends over the last two decades. The compatibilization of starch and synthetic biodegradable polymers increases the water resistivity and mechanical properties, such as tensile strength and percentage elongation at break, melting and thermal degradation temperatures, and barrier properties. Starch/polymer blends can also be tailored to enhance biodegradability, thermo-mechanical and good

processing properties, making them available for a wide range of applications. These starch/polymer blends show potential in large-scale food packaging applications replacing petroleum-based single-use plastics.

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