



# **Progress in Starch-Based Materials for Food Packaging Applications**

Lucia García-Guzmán <sup>1</sup>, Gustavo Cabrera-Barjas <sup>2</sup>, Cintya G. Soria-Hernández <sup>3</sup>, Johanna Castaño <sup>4,</sup>\*, Andrea Y. Guadarrama-Lezama <sup>1</sup> and Saddys Rodríguez Llamazares <sup>5</sup>

- <sup>1</sup> Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón esq. Paseo Tollocan s/n, Col. Residencial Colón, Toluca 50120, Mexico; Igarciag018@alumno.uaemex.mx (L.G.-G.); avguadarramal@uaemex.mx (A.Y.G.-L.)
- <sup>2</sup> Unidad de Desarrollo Tecnológico, Parque Industrial Coronel, Universidad de Concepción, Concepción 3349001, Chile; g.cabrera@udt.cl
- <sup>3</sup> Tecnológico de Monterrey, School of Engineering and Sciences, Ave. Eugenio Garza Sada 2501, Monterrey 64849, Mexico; cintya.soria@tec.mx
- Facultad de Ingeniería y Tecnología, Universidad San Sebastián, Lientur 1457, Concepción 4080871, Chile
   Centro de Investigación de Polímeros Avanzados (CIPA), Avenida Collao 1202, Edificio Laboratorio-CIPA,
- Concepción 4081112, Chile; s.rodriguez@cipachile.cl
- \* Correspondence: johanna.castano@uss.cl

**Abstract:** The food packaging sector generates large volumes of plastic waste due to the high demand for packaged products with a short shelf-life. Biopolymers such as starch-based materials are a promising alternative to non-renewable resins, offering a sustainable and environmentally friendly food packaging alternative for single-use products. This article provides a chronology of the development of starch-based materials for food packaging. Particular emphasis is placed on the challenges faced in processing these materials using conventional processing techniques for thermoplastics and other emerging techniques such as electrospinning and 3D printing. The improvement of the performance of starch-based materials by blending with other biopolymers, use of micro- and nano-sized reinforcements, and chemical modification of starch is discussed. Finally, an overview of recent developments of these materials in smart food packaging is given.

Keywords: starch-based materials; formulation; processing; food packaging

## 1. Introduction

The overexploitation of natural resources and accelerated climate change has led industries to incorporate more environmentally friendly materials and technologies into their processes. Hence, the food packaging industry is increasingly looking to replace petroleum-based materials in single-use applications. Until 2019, world plastics production reached 368 million tons [1], of which 40% corresponds to food packaging and take-away food [2]. The main reasons why plastics have been the most widely used materials for such applications are their low cost of production, higher versatility, good barrier properties to water and gas permeability, as well as their mechanical and optical properties [3]. However, the accumulation of waste, which interferes with the natural dynamics of ecosystems, has had a particularly negative impact on the environment in the case of plastics due to their high durability and difficult degradation (up to 400 years) and this has stimulated research towards the development of new biodegradable materials [4].

Biopolymers are considered the best solution with regard to replacing synthetic plastics as, although they present similar characteristics, they possess a short biodegradation time and good biocompatibility with other materials and high availability. During the last decade, world biopolymer production has increased to 2.1 million tons in 2018 [5]. The Nova-Institute predicts that by 2023 this will amount to 2.62 million tons [1], which opens



Citation: García-Guzmán, L.; Cabrera-Barjas, G.; Soria-Hernández, C.G.; Castaño, J.; Guadarrama-Lezama, A.Y.; Rodríguez Llamazares, S. Progress in Starch-Based Materials for Food Packaging Applications. *Polysaccharides* **2022**, *3*, 136–177. https://doi.org/10.3390/ polysaccharides3010007

Academic Editor: Guillaume Pierre

Received: 1 December 2021 Accepted: 11 January 2022 Published: 14 January 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). up opportunities to overcome resource depletion and plastic pollution. A wide range of materials are used in the production of biodegradable polymers such as starch, cellulose, chitosan and proteins [6], among the most used are starch and cellulose for the manufacture of food packaging for their biodegradability, non-toxicity, low cost, abundance in nature and renewability, all of which make them ideal candidates in the development of sustainable materials [7,8].

Starch is not a thermoplastic material, however in the presence of plasticizers (water and polyols), heat and under shear stresses or in their absence it behaves as a thermoplastic. Plasticization of the starch granule by extrusion leads to structural disruption and diffusion of the plasticizer. Starch is incorporated in the form of granules or in gelatinized form in film formulations manufactured by thermoplastic material transformation processes [9,10]. These films have the disadvantage of moisture sensitivity; to reduce these disadvantages, starch has been blended with other synthetic or biodegradable polymers such as PLA, or chemically modified [11,12]. Different starch-based materials are available on the market under the brand names Mater-Bi<sup>®</sup>, Bioplast and Biopolar. The properties of starch-based materials depend, among other factors, on the botanical source, crop conditions and genetic variety where the starch is extracted from. The aim of this review paper is to review the evolution in the preparation, modification, and processing of starch-based materials for food packaging applications. Figure 1 shows a schematic of the structure, modifications and processing techniques studied in the evolution of starch-based materials.



**Figure 1.** Schematic illustration of the structure, modifications and processing techniques of starchbased materials. The images were taken from various sources: Starch granule [13]; acetylation starch film [14]; plasticization starch [15]; solve casting and 3D printing [16]; and blend and nanocomposite starch [17].

## 2. Starch

Starch is a natural, renewable, and biodegradable polysaccharide produced by many plants during photosynthesis as a source of stored energy [7,18]. Starch is the second most abundant organic substance found in nature and serves as the major conserved carbohydrate in plants. Starch can be isolated from various sources such as cereal grains

(considered the main source of obtaining), some roots, tubers [19], fruit stones [20], and rhizomes [21]. Starch extraction is carried out by simple and economical methods. The main stages involved in the extraction of starch granules by wet extraction are washing, milling, extraction, decantation and drying [13].

Starch is a multi-scale structure consisting of amylose and amylopectine macromolecules. Amylose is a linear polymer consisting of glucose units linked through  $\alpha$ -(1,4) glycosidic bonds and amylopectin, the major component, has a branched structure, with a linear main chain composed of glucose units linked by  $\alpha$ -(1,4) bonds and the branched chains formed through  $\alpha$ -(1,6) glycosidic bonds. The short chains of amylopectin with a degree of polymerization (DP) greater than 10 form the double helices responsible for the crystallinity of the starch granule [22,23]. The crystalline region in the starch molecule is believed to have been formed by the crosslinking of amylopectin side chains, while amylose is found in the amorphous region of the granule as a single molecule randomly interspersed between amylopectin molecules [24].

Starches can be classified according to the amylose/amylopectin ratio; thus, so-called "waxy" starches contain less than 5% amylose, "normal" starches between 20–30% amylose and "high amylose" starches have amylose contents equal to or higher than 40% [25,26]. The starch from cereals, tubers and pulses has around 15–33%; 15–30%, and 25–50%, respectively, of amylose content [27,28]. In the case of cereals, the amount of amylose they present is accompanied by lipids with amylose, while roots and tubers have little or no lipid [29].

The shape, size, composition and molecular structure of starch granules depend on their botanical origin, period of formation and growing conditions [30]. Starch granules have different shapes: Spherical, oval, polygonal and lenticular. Starch granule size and shape is an important feature, and the granules appear in many different forms. The starch granule size varies from 1 to 110 mm in diameter and exhibits a round, or lenticular to polygonal shape. Furthermore, they also present a high degree of polymerization and crystallinity with repeating glucose linked by  $\alpha$ -glycosidic bonds [23,29]. Table 1 summarizes the characteristics of cereal, tuber, pulse and no conventional source of starches grains. Thus, for example, cereal starches have different grain shapes, their amylose percentage is in the range 15–27% and their structure is of type A (monoclinic).

Clasification						
Source	Source of Starch	Geometry	Size (µm)	Amylose (%)	Structure Type	Reference
	Buckwheat (Fagopyrum esculentum)	Polygonal	5–8	-	А	[31]
	Amaranth	Polygonal	1-2.5	4	А	[32]
	Normal maize Waxy maize Rice White Rice red Rice black	Angular	15–20	3–40 1–3	А	[33]
Cereal		Polygonal and angular	-	18–20 24–26 20	А	[34]
	Wild-type wheat starch High-amylose wheat starche	Spherical Deformed and heterogeneous shapes of granules	-	32 71–84	A B	[35]
	Canary seed CDC maría C05041	Polygonal	2–3 2.4	23–25 22–24	А	[36]

Table 1. Characteristics and source of starch granules.

Clasification						
Source	Source of Starch	Geometry	Size (µm)	Amylose (%)	Structure Type	Reference
	Amadumbe corms purple and white	Irregular and polygonal	1–6	7.5	А	[37]
Tuber	Arracacia xanthorrhiza Oxalis tuberosa Sweet potato Yellow sweet potatoes	Oval and circular circular and polyhedral circular and polyhedral	5–15 10–30 5–20	22 31–33 41–43	-	[38]
	Qin5 Qin 9 12-18-28 Shang 19 Orange sweet potatoes Su16 Qin 8 Purple sweet potatoes Qinzi 2, Quinzi 3	The eight starch granules of sweet potato were similar, exhibiting round, polygonal, oval, semi-oval, and hemispherical shapes with different sizes.	17–18 16–17 20–22 20–22 22–24 20–22 20–22 21–24	23 20 23 18–21 19 25 21 23	C type: Qin 8, Qin 9, Qingzi 2, 12-18-28, Qingzi 3, and Su 16, and A type for Shang 19 and Qin 5.	[39]
	Arisaema elephas Buchet Arisaema yunnanense Buchet Arisaema erubescens (Wall.)	Three starches all had spherical, irregular and truncated shapes with central hila.	3.0–5.0	29 28 32.0	C <sub>A</sub> C <sub>A</sub> A	[19]
	Chayote tuber starch	Oval, irregular, truncated and rounded	7–50	13	-	[40]
	Curcuma aeruginosa Curcuma amada Curcuma aromatica Curcuma caesia Kaempferia parviflora Zingiber montanum	Elongated, elliptical, oval, polygonal, cuboidal and spheroid	6–25 10–30 5–28 8–30 2–15 5–20	22 23 25 28 24 23	В	[41]
Pulse	Pea Lentil Faba bean	Oval, kidney and irregular shapes	10-45	40–42 38–40 39–40	С	[42]
	Chickpea	Round shape	9–70	36–41	С	[43]
	Babassu mesocarp Cashew nut shell	Polygonal Irregular in shape and size Trigonal, tetragonal,	-	26–28	C B	[44] [45]
No	Jackfruit seed	round, semi-oval, and bell shape.	3–15	32–34	А	[46]
conventional	Loquat ( <i>Eriobotrya japônica</i> ) seed	Oval and cylindrical	29–45	15–46	С	[47]
	Avocado seeds (Persea americana Mill)	Oval and ellipsoid	10-44	30–31	В	[48]
	Chesnut Pehuen	Oval and ellipsoid Spherical	15–22 12–21	15–20 38–40	B C	[49] [13]

	Tabl	le 1.	Cont.
--	------	-------	-------

Most of the reported works related to starch focus on wheat [50], corn [6], potato [39], and rice starches [34], due to their commercial importance. However, there is increasing interest in studying new non-conventional starch sources to produce bio-based and/or compostable materials such as pehuen [13], chesnut [49], jackfuit seed [46], avocado seed [48], pea, lentil, faba bean [42], and chickpea [43] among others.

The crystalline arrangement of the double helices generates three X-ray diffraction patterns for starch, known as type-A, type-B and type-C [51]. The type-A polymorphism is characteristic of most cereals; the amylopectin double helices are packed in the form of monoclinic unit cells and contain 4–8 water molecules (this packing being denser than that of type-B). In this polymorphism, the chains are short with a degree of polymerization (DP) between 11 and 16 [52]. The type-B polymorphism, usually found in tubers and roots, presents hexagonally packed double helices with 36 water molecules when hydration is 27%. In type-B polymorphism the amylopectin chains, which form the double helices, are long with PD between 30 and 45 [53]. The C-type polymorphism is a mixture of type

A and B polymorphism, characteristic of leguminous starches. At low humidity, high temperature and pressure can cause a structural transition from type B to type A to occur; this transition is due to water loss, which causes reorganization of the double helices [54]. The crystalline structure of the grain influences the physicochemical properties of starch. Thus, for type-A starches, the gelatinization temperature tends to increase as the degree of crystallinity increases, whereas for type-B starches, this parameter decreases with an increasing degree of crystallinity in the granule [55]. In addition, it has been reported that the percentage of crystallinity in starch granules is inversely proportional to amylose content [56–58]. Tester et al. [26] found that in pea starches with C-type polymorphism, the center of the granule is rich in B-type polymorphism, whereas the peripheral regions are rich in A-type.

## **3.** Chronology of the Development of Starch-Based Materials for Industrial Applications

Starch is an attractive raw material for non-food industrial applications as it is widely available, cheap, biodegradable, and uniquely granular. However, the swollen granules cannot retain their swollen structure and collapse instantaneously. Starch materials have limited industrial applications due to their high hygroscopicity, poor mechanical properties and syneresis [59]. Hence, at least three generations of starch-based materials can be distinguished (Figure 2): Traditional, where the development of thermoplastic starches was achieved; Transitional, where physical and chemical modifications, blends with other polymers and industrial scale processing were possible; and, Nanostructured. Several strategies have been reported to improve the performance of starch-based materials in humid environments. For example, starch can be blended with a hydrophobic polymer, such as poly(lactic acid) and polyhydroxybutyrate to increase its hydrophobicity [60–62]. However, these blends have poor mechanical properties and high starch contents [13]. Incorporating natural fibers into starch-based materials also reduces their water uptake, however these materials also require a high fiber content to decrease their hydrophilicity [63,64]. Another way to improve starch based materials' properties through chemical or physical modification. This can be achieved by reducing its hydrophilicity and tendency to dissolve in water via esterification of OH groups of  $\alpha$ -D-glucan with methylene groups [65,66]. Currently we are in the most advanced generation, where new processing techniques and modifications and the manipulation of matter at the nanometer scale have all been achieved and, as such, have enabled the creation of high performance materials.



Figure 2. Evolution of starch-based materials.

## 3.1. Modification of Native Starches

## 3.1.1. Thermo-Plasticization

Starch is not a thermoplastic material, however, in the presence of plasticizers (water and polyols), heat (90–180 °C) and with or without shear stress, it presents thermoplastic properties. The transformation of starch to a thermoplastic depends on gelatinization. In this irreversible process, the starch granules lose their crystalline arrangement, swell, and become unstructured. In addition, the partial separation of starch components occurs as the amylopectin double helix unwinds and dissociates and amylose separates from amylopectin [22,67]. The loss of crystalline order produced in excess water (>63%) is mainly due to the penetration of water into the granule, causing a decrease in the interand intramolecular interactions of starch components. Heating in the water damages the crystalline structure of the starch granules and makes amorphous amylopectin [68]. During the processing of thermoplastic starches (TPS), several thermal transformations related to gelatinization occur, e.g., water diffusion, starch granule expansion, melting and crystallization [69]. Poor mechanical properties and higher hydrophilic are some of the characteristics of TPS that make it unsuitable for various applications, like food packaging materials. For this reason, several modifications have been explored in order to modify their properties. The incorporation of reinforcements, chemical modification and blending with other polymers are the main ways to improve the positive attributes or minimize the defects of starch-based materials.

## 3.1.2. Chemical Modifications

Chemical modifications of starches are carried out by the incorporation of functional groups into the starch macromolecules (breaking of glycosidic bonds), leading to partial or total disruption of the physicochemical properties such as structure, compositions, gelatinization, retrogradation, and pasting characteristics. The main chemical modifications made to starch are reduction (oxidation, hydrolytic, enzymatic) [70], substitution (etherification, esterification) [63,64] and crosslinking (di ether, di ester) [71].

Starch substitution is a method of modification, in which a portion of the hydroxyl groups of anhydro-glucose units that constitute the starch chain is changed to other groups such as acetyl group, thereby changing the molecular structure of the starch. There have been reports that state starch esterification with organic acids and acid anhydrides reduces retrodegradation and improves the physicochemical properties of TPS used in the plastics industry, specifically in the packaging sector [72–74]. Thus, for example, Lopez et al. [75] concluded that films made from previously acetylated corn starch reduced water vapor permeability and increased the percentage of elongation at break with respect to films made from unmodified starch; in addition, modified starch films were more easily heat sealed. The most commonly used esterifying agents are formic acid, acetic acid, propanoic acid, butanoic acid, maleic acid and the corresponding anhydrides [76]. The mechanism of starch esterification with anhydrides is based on a nucleophilic substitution reaction.

Starch reduction is a modification method that consists of generating more functional groups, for example in starch oxidation, carbonyl and carboxyl are introduced in the starch modified by reduction, hence its functionality and reactivity increase. A decrease in swelling capacity and viscosity of the paste has been reported when starch was modified by reduction [77]. Sandhu et al. [78] compared the physicochemical properties of a waxy corn starch with those of a starches chemically modified by oxidation using sodium hypochlorite as the oxidizing agent. Significantly different results were reported for oxidized modified starch, which showed decreased swelling power, solubility, and gelatinization enthalpy, however showed increased pasting viscosity as compared to its native starch. Depending on the reactive oxidants used for chemical modification and starch source, the final products are different, with independent properties [79]. The main reactive oxidants used in starch modification include hydrogen peroxide, potassium permanganate, sodium hypochlorite, per-acetic acid, chromic acid and nitrogen dioxide.

Starch crosslinking is a method of modification, in which a linear or branched chains are covalently interconnected. The crosslinking of starches enhances the hydrophobicity and structural stability of the granules, thus improving their hydration properties. Sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), epichlorohydrin (ECH) and phosphorus chloride (POCl<sub>3</sub>) and acid have been used in the chemical modification of starch by crosslinking [80]. However, glutaraldehyde and epichlorohydrin are not considered safe due to the risk that they are hazardous to health due to their toxic and irritant nature [81]. Citric acid is one of the most widely used crosslinking agents in starch granule modifications as, due to its carboxyl groups, it can react with the hydroxyl groups of starch molecules to form intermolecular diester-covalent bonds, and it is inexpensive and non-toxic. In addition, it has been shown to increase film stability during storage [82] and to reduce water vapor transmittance in starch-based materials [83]. The effects of chemical modification using sodium tripolyphosphate (STPP) and sodium phosphate (STMP) on oat starch was investigated by Berski et al. [84]. The results reveal that the amount of amylose decreased after modification, which was attributed to partial depolymerization of amylopectin and the release of sufficient long chains to create a color complex with the iodine reagent. In addition, an increase in the swelling capacity and viscosity were observed. Table 2 summarizes the main chemical and physical modifications of starches.

Table 2. Chemical and physical modifications of starches.

	Physical Mo	difications		Chemical Modifications			
Source of Starch	Treatment	Conditions (Time/Temp)	Reference	Source of Starch	Treatment	Conditions (Time/Temp)	Reference
Metroxylon sagu	Microwave heat	15 min at 4 °C	[85]	Corn	Branching enzyme treatment	99 °C for 15 min	[86]
Horse Chestnut seeds	Heat-moisture	110 °C for 3 h	[87]	Horse Chestnut seeds	Acid hydrolysis	50 °C for 30 min	[87]
Corn	Heating in evaporating dishes	210 $^\circ \text{C}$ for 30 min	[88]	Potato	Acetylation	pH 8, 30 °C stirred for 1 h	[89]
Wheat	Superheated steam	130 °C, 150 °C and 170 °C for 1 and 4 min	[90]	Oat and Barley	Oxidation	10 g Cl for 1 kg of starch using N <sub>A</sub> ClO, milled for 50 min	[91]
Corn	Repeated dry-heat (RDHT)	Cycles of 140 °C for 4, 8, 12 and 16 h and 1 h of cooling	[92]	Corn	Octenyl succinic anhydride modification	pH 8, 35 °C, stirred for 3 h	[88]
Pea and lentil cultivar	Hydrothermal	120 °C for 24 h	[93]	Wheat	Cross-linking	Stirring at 170 rpm, 40 °C for 80 min	[94]
Barley	Annealing (ANN)	50 °C for 72 h	[95]	Rice starche	Esterification (octenylsuccinic anhydride (OSA) Esterification	2 h	[96]
Amaranth	Heat-moisture	150 mL min <sup>-1</sup> , 130 °C	[97]	Rice starch	(octenylsuccinic anhydride (OSA)	35 °C, 5 h	[98]
Mango kernel	Heat-moisture	3 h at 110 °C with occasional shacking	[99]	Quinoa starch	(octenylsuccinic anhydride (OSA)	35 °C, 3 h	[100]
Wheat	High hydrostatic pressure	300, 400, 500, 600 MPa; 20 °C for 30 min	[101]	Waxy cassava starch	Esterification (octenylsuccinic anhydride (OSA)	24 h	[102]
				Sago starch	(octenylsuccinic anhydride (OSA).	9.65 h	[63]
				Ginkgo starch	Esterification (octenylsuccinic anhydride (OSA)	35 °C, 8 h	[64]
				Sorghum and maize Waxy starches	Esterification octenylsuccinic anhydride (OSA)/β-amylase	-	[103]
				Waxy maize starch	Cross-linking	40 °C, 4 h	[71]
				Waxy maize starch	Cross-linking	40 °C, 4 h	[104]
				Native potato starch	Cross-linking	30 °C, 20 h	[105]

Physical Modifications					Chemical Modific	ations	
Source of Starch	Treatment	Conditions (Time/Temp)	Reference	Source of Starch	Treatment	Conditions (Time/Temp)	Reference
				Tapioca starch	Cross-linking	30 min	[106]
				Carboxymethyl starch	Grafting	-	[107]
				Native corn-starch	Chemically grafting	130 °C, 24 h	[70]
				Corn starch	Grafting (DMSO)	50 °C, 36 h	[108]
				Normal maize starch	Citric acid	room temperatura, 12 h	[109]
				Corn	Debranching by pullulanse	55 °C for 1.5 h	[110]
				Corn	Hydroxipropilation	pH 11.5, 20 h with stirring	[110]
				Sorghum	Acid Hydrolysis	40 °C, stirring 1h	[111]
				Sorghum	Oxidation	40 °C, pH 9.5, 30 min	[112]
				Potato starch	Acetylation	115°C, stirring for 5 h	[113]
				Cassava	Ozonation	gas flow of 1 L·min <sup>-1</sup> , ozone concentration 41 mg O <sub>3</sub> ·L <sup>-1</sup> , 25 °C for 15 and 30 min	[114]
				Broken rice	Succinylation	pH 9–9.5, addition of 2%, 4% and 5% of anhydride	[115]
				Rice starch	Acetylation	90 °C, 10, 30 and 90 min	[116]

 Table 2. Cont.

## 3.1.3. Physical Modifications

Recently, non-thermal treatments have gained relevance due to the minimal amount of energy required and environmental sustainability (Table 3). Also, these technologies represent great modifications or changes in the material properties. Some of the treatments influence the physical properties of starches. In this context, high hydrostatic pressure treatments influence the gelatinization and crystallinity patterns of starches [101]. The ozonation results in the disruption of starch granules influencing the particle size and weight increasing the crystallinity [114]. Non-chemically-modified starch that functions like chemically-modified starch is of great interest. Non-thermal technologies also have an effect on the chemical properties and it has been found that plasma applications indicate chemical changes, including crosslinking in the starch molecules, modifying the thermal transitions such as melting temperature and enthalpy [117,118].

Table 3. Non-thermal treatments modification in starches.

	Non-Thermal Treatments								
Source of Starch	Treatment	Conditions (Time/Temp)	Reference						
Modified Starch RS4	Ultrasound	2 s pulses, 30 min, 25 °C	[119]						
Corn	UV irradiation	$2.88 \text{ J/cm}^2$ for 30 min	[88]						
Corn	Electron beam irradiation	6.23 MeV, 75 mA, 100 Hz, pulse duration of 3.5 μs,	[120]						
Corn	Corona electrical discharges	25 kV, 50 Hz, pulse duration of 100 ns, during 5 min	[120]						
Barley	High pressure	400, 450 and 500 MPa at 75 $^{\circ}\mathrm{C}$	[95]						
Wheat and potato	Pulse electric field	Pulses at 10, 15, 20, 25 and 30 kV, 600 Hz, 6 μs pulse width	[121]						

	Non-Thermal Treatments								
Source of Starch	Treatment	Conditions (Time/Temp)	Reference						
Таріоса	Irradiation	Gamma Cell 5000, doses of 0, 5, 10 and 20 kGy	[122]						
Corn Corn	Plasma HMDSO plasma	20 rpm, 90 W during 30 min $4.5 \times 10^{-1}$ mbar pressure, 30 min, 70 W	[118] [117]						

Table 3. Cont.

The ultrasound treatments are under the influence of strong shear force, high temperatures (reached by ultrasound waves application), which influence the properties of the starch and inherently the applications. The changes in starch depend on frequency, intensity, and the amount of time ultrasound was applied, and also the source of starch. Usually, ultrasound treatments cause damage to the starch granule, pores, fissures and cracks. At the molecular level, changes in the amylose and amylopectine molecules function as part of the experimental conditions. This structural change affects the physicochemical properties of the starch. Several research works show that a clear tendency or pattern to the modification of physicochemical properties of starch treated by ultrasound does not exist. This means in some cases an increase or decrease in gelatinization, retrogradation swelling, pasting properties and viscosity. Rather, all these properties are the consequence of the source, type and structure of starch, the intensity and duration of ultrasonication, and the temperature and water content of the starch [123–126].

Some differences and modifications in time of treatments, pulses and intensity are reported on starch modifications under PEF (Pulsed Electric Fields). However, most of the research focused on PEF application that referred to damage to the starch granule, a greater agglomeration of granules, the reduction in its relative crystallinity, a breakdown in viscosity, the reduction in gelatinization temperature, and an alteration to the birefringence [121,127–130].

## 3.2. TPS Blends whit Biodegradable Polymers

## 3.2.1. Poly (Lactic Acid) (PLA)

PLA is an aliphatic polyester produced through the polymerization of lactic acid obtained from sugar and beets [131]. Categorized as a Generally Recognized as Safe (GRAS) by the Food and Drug Administration (FDA), this material is suitable to be applied in food and beverage packaging [132]. Starch is blended with PLA to reduce the PLA cost and to improve the biodegradation properties. However, both polymers have different polarities, which limit their compatibility due to low barrier and mechanical properties [62,133]. Hence, several studies are focused on improving the compatibility of PLA and TPS [61,134,135]. The compatibilizers of PLA blends mainly include non-reactive compatibilizers, reactive polymer compatibilizers or active small molecular substances, and in situ form block copolymers or graft copolymers. The common principles and characteristics of compatibilization for PLA/starch blends were studied by Zeng et al. [136]; Nagarajan et al. [137]; and Li et al. [138]. Gurler et al. [139] examined the effects of crosslinker reagent (3-(Aminopropyl) trimethoxy silane) and the bilayer film material of PLA/starch blend. The results achieved revealed that they have beneficial properties for protecting the environment and are applicable to food packaging. TPS prepared from modified graft starches have been shown to reduce TPS hydrophilicity, resulting in enhanced compatibility with PLA. Thus, PLA-gMTPS could act as a compatibilizer by reducing coalescence and surface tension of the TPS phase during blending [140]. However, an excessive coupling agent may act as plasticizer and be responsible for the decrease in the maximum tensile strength. Noivoil and Yoksan [61] substituted the cassava starch with acetylated cassava starch PLA/TPS modified films, which may be used as flexible packaging where biodegradability and short-term use are needed.

## 3.2.2. Poly (Butylene Adipate-Co-Terephthalate) (PBAT)

PBAT is an aromatic-aliphatic copolyester and a typical example of biodegradable polymeric materials from petrochemical resources [141]. The physical and mechanical properties of PBAT are close to those of polyethylene. However, the application of PBAT in some fields is limited due to the high cost. Wei et al. [142] demonstrated that by modifying the starch (SMGs), using commercial compatibilizer (Joncryl-ADR-4368) and an adequate ratio of the components (PBAT/M-PBAT/TPS: 40/20/40), excellent physical and mechanical properties of PBTA/starch blends are achieved. Recently, Leelaphiwat et al. [60] studied Nisin and EDTA as compatibilizers in PBAT/TPS blends by blown-film extrusion for active packaging applications. Their results shown Nisin improved the compatibility of starch and PBAT films, which increased smoothness, while EDTA increased hydrophilicity and the oxygen barrier of PBAT/TPS films; active films with EDTA reduced microbial growth in chilled meat up to 1.4 log and Nisin and EDTA stabilized redness and delayed lipid deterioration in packaged pork. PBAT/TPS-based biodegradable packaging containing sodium benzoate (6%) and potassium sorbate extended the shelf-life of packaged rice noodles by delaying Aspergillus niger and Rhizopus sp. growth [143]. The incorporation of maleate PBAT and citric acid (2%) on PBAT/TPS blends were investigated by Fourati et al. [144]. They observed a much improved strain at break, which could be due to their use of a phase inversion, with the TPS phase being the continuous matrix and PBAT the dispersed phase.

### 3.2.3. Polyvinyl Alcohol (PVA)

PVA is a synthetic polymer highly soluble in water, which for this reason has been widely used in the textile industry in the preparation of stabilizers and thickeners. PVA also possesses good chemical resistance and high mechanical properties although its disadvantages include a limited barrier and thermal properties and relatively high cost [145]. In addition, it possesses high compatibility with other polymers, and for this reason is often mixed with starch in order to form biocomposites [146,147]. The TPS films show weak mechanical properties, and higher degradation due to decomposition when compared to TPS film added with PVA.

Table 4 shows several works where it is possible to observe that when PVA was added to the mixture, the mechanical properties of the films were improved. Ismail and Zaaba [148] reported a remarkable increase in the tensile strength of the blend films, which indicated the presence of intermolecular interactions of the components by way of hydrogen bond formation, which strengthened the bonding of the PVA with sago starch. Syamani et al. [149] reported that the addition of 25% polyvinyl alcohol (PVA) into bioplastic made from modified cassava starch produced a bioplastic with higher tensile strength compared to that without PVA addition. On the other hand, the addition of 100% PVA could slightly increase bioplastic elongation. The decomposition temperature of bioplastic made from modified cassava starch with the addition of 50% PVA was higher than of that without PVA addition, which indicated that it was more thermally stable. In terms of food packaging, the permeability at water vapor content and water adsorption are important issues when deciding upon applications. More of the works reporting PVA/starch films are not reporting adsorption of water or permeability at water vapor, and there is little information regarding this (Table 4). This mix is less hydrophilic than other film mixtures, such as PLA/starch.

Blend System	Starch Source	Modifier	Processing Method	Tensile Strength (MPa)	Water Vapor Permeability (g/m Pa s)	Reference
PLA/Starch	Potato	Crosslinking with 3-(Aminopropyl) trime-thoxy silane (3-APTMS)	Films casting	$11 \pm 2$	$15\pm0.5$	[138]
PLA/Starch	Tapioca	-	Extrusion	$8\pm 2$	-	[62]
PLA/Starch	Corn	Maleic anhydride (MA) and epoxidized cardanol (Epicard)	Extrusion	$25\pm12$	-	[135]
PLA/Starch	Corn	Poly (ether block amide) (PEBA)	Reactive blending	$22\pm 2$	-	[134]
PLA/Starch	Casava	maleic anhydride	Extrusion	$4\pm1.0$		[150]
PLA/Starch	Casava	PLA-g-TPS	Extrusion	$6 \pm 1.0$		[140]
PLA/Starch	cassava	Acetylated starch	Twin-screw extruder	$23\pm4$	$8\pm1.0$	[61]
PBAT/starch	Casava	nisin-ethylenediaminetetraacetic acid (EDTA)	Blown-film extrusion	$20\pm10$	$2\pm1.0$	[60]
PBAT/starch	Potato	Joncryl-ADR-4368,ynthesized reactive compatibilizers, SMGs	Extrusion	$20\pm 8$	-	[142]
PBAT/starch	Potato	Maleic anhydride (MA), citric acid (CA)	Extrusion	$10 \pm 1$ (MA), $5 \pm 2$ (CA)		[151]
PBAT/starch	Cassava starch	Sodium benzoate (SB) and potassium sorbate (PS)	Blown-film extrusion	$10\pm4$	$2\pm1.0$	[143]
PBAT/starch	Tapioca	Maleic anhydride and benzoyl peroxide	Reactive extrusion	$10 \pm 3$		[152]
PVOH/starch	Ċorn	Photo crosslinking with sodium benzoate	Film casting	16–20 MPa	NR	[153]
PVOH/starch	Corn	Citric acid (co-plasticizer)	melt-blending	NR	NR	[154]
PVOH/starch	Corn	Glutaraldehyde	Casting	7.8–13.7 MPa	NR	[155]
PVOH/starch	Corn	Glacial acetic acid as a crosslinking agent	Casting	5–240 MPa	NR	[156]
PVOH/OH	Cassava	Acetate solution	Casting	1.35–13.03 MPa	NR	[149]
PVOH/starch	Tapioca	Supercritical CO <sub>2</sub>	Injection molding	20–25 MPa	NR	[157]
Chitosan/starch	Ċorn	-	Casting	10–40 MPa	-	[158]
Chitosan/starch	Tapioca	-	Casting	-	$2.8  ext{}12.1  imes 10^{10}$	[159]
Chitosan/starch/mustard oil	Potato	2-hydroxyethyl methacrylate (HEMA)	Casting	1.7–13 MPA	-	[160]
Chitosan/starch	NR	Glutaraldehyde	Casting and solvent evaporation method	NR	15.57–16.57 (g/m <sup>2</sup> h)	[161]
Chitosan/starch	Corn	-	Casting	3.44–19 MPa	NR	[162]
Chitosan/starch	corn	-	Casting	1.6–73 MPa	$1.4-2.5 (g/m^2 h kPa)$	[163]
PCL/starch	Meritena (corn), Waxy, Amarant and GelInstant	-	Extrusion	NR	100–1800 MPa	[164]
PCL/starch	NR	Maleic anhydride and clav	Extrusion	NR	7–40 MPa	[165]
PCL/starch	Corn	-	Pressing and molding	NR	NR	[166]
PCL/starch	NR	-	ND	NR	NR	[167]
PCL/starch	Corn	-	Molding	NR	5–29 MPa	[168]
PCL/starch	NR	Maleic anhydridegrafted-polyethylene	Mixing	NR		[169]

 Table 4. Blend system and characteristics of starch-based materials.

Table 4. Cont.

Blend System	Starch Source	Modifier	Processing Method	Tensile Strength (MPa)	Water Vapor Permeability (g/m Pa s)	Reference
TPS/Natural Rubber	Corn	Natural latex	Mixing	0.7–9 MPa	NR	[170]
TPS/Natural Rubber	Corn	Oxidized natural rubber (ONR)	Extrusion	0–4 MPa	NR	[171]
TPS/Natural Rubber	Potato	Natural rubber (NR) and epoxidized natural rubber (ENR)	Compressing and molding	1–9 Mpa	NR	[172]
TPS/Natural Rubber	Cassava	Epoxidized natural rubber (ENR)	Melt blending, molding and compressing	0–2.5 MPa	NR	[173]
TPS/Natural Rubber	Cassava	Rubber wood sawdust (Hevea brasiliensis)	Compression and molding	0.33–1.23 MPa	NR	[174]
TPS/Natural Rubber	Sago	Natural rubber latex	Compression and molding	4.46–25.2 MPa	NR	[175]
TPS/Natural Rubber	Cassava	Natural rubber latex	Casting	4–8.5 MPa	NR	[176]
TPS/PE	Corn	Maleic anhydride (MAH	Bleeding and extrusion	3.8–9.0 MPa	NR	[177]
TPS/PE	Potato	random ter-polymer of ethylene, acrylic and maleic anhydride	Blown film extrusion	7–22 MPa		[178]
TPS/PE	Rice and potato	-	Mixing and extrusion	3.04–8.34 MPa	$\begin{array}{c} 0.1160 \ (\text{g m}^{-1} \ \text{s}^{-1} \ \text{Pa}^{-1}) \\ \times \ \text{l0}^{-13} \end{array}$	[179]

NR: Not reported.

Sometimes the hydrophobic nature of the mixed film of TPS-PVA still needs to be improved and for this reason nanofibers are added [180]. Some research works showed the addition of nanofibers or nanoparticles improved the water uptake of films. Heidarian et al. [181] reported an increase in the moisture penetration of films when the concentration of nanofibers was increased up to 10%. This was attributable to the imperfect morphology developed by the composite films due to the aggregations, cavities and voids presented by addition. On the other hand, addition of nanoparticles also has influenced the low water content. Keshk et al. [182], reported that the addition of magnetic particles in composite films manifested lower water vapor transmission, thus it can be concluded that MNPs improve the hydrophobicity. This research is in line with that reported by Fahma et al. [183] and Fahma et al. [184] who reported the difficulty of water vapor penetration into obtained nanocomposite films caused by the strong hydrogen bonding between cellulose nanofibers and TPS-PVA matrix.

## 3.2.4. Chitosan

The films prepared with a blend of chitosan and TS are preferred, due to their mechanical properties (tensile strength and elongation at break), to films that are only enhanced with chitosan [158,161]. Pavoni et al. [157] reported that these mechanical properties are the result of the formation of intermolecular hydrogen bonding between  $NH_3^+$  of the chitosan backbone and OH<sup>-</sup> of the starch. This enhancement in mechanical properties may be favorable in terms of resistance of biodegradable materials. On the other hand, in presence of glycerol as plasticizer there is a decrease in tensile strength, and an increase in elongation at break due to the plasticization phenomena. The addition of glycerol promoted the interactions among chitosan, starch and glycerol through hydrogen bonding and proved the strong interactions (decrease in glycerol mobility) occurring among starch, chitosan and glycerol [162]. In this way, new formulations can be prepared to select it as food packaging materials with the most desirable characteristics, not only to protect the foods but also in terms of the biodegradability of materials. In this context, the addition of glycerol reduces the tensile strength, for example Xu et al. [158] referred 40 MPa as the maximum value reported for films, meanwhile, Liu et al. [162] reported almost the half of this value (19 MPa). Also in presence of chitosan there exists a decrease in water vapor transmission rates and the crystalline structure is depressed in the presence of starch.

#### 3.2.5. Polycaprolactone (PCL)

The polycaprolactone is an aliphatic polyester biodegradable with a low melting point (60 °C) compared with other polymers and a thermal transition temperature around of -60 °C [159]. Few research works are made in the blend of PCL/TS. This is probably due to the PLC being a highly biodegradable polymer. Most of the works focus on the addition of fibers and additives to give reinforcement.

The simple blend of PCL with starch did not cause significant changes to the mechanical properties of films such as tensile strength and elongation to break [164]. It seems to be that the physicochemical characteristics (especially the mechanical properties) of the PCL/TPS blend are dependent on the type of starch used. In addition, the gelatinized starch made the blends more fluid, increased the absorption of water, reduced the crystallinity of PCL, and maintained a good dispersion of the blends [166]. Also, it has been reported that the mechanical and thermal properties of PCL became noticeably worse when it was blended with starch, due to the poor compatibility between the two phases [169].

## 3.2.6. Other

Blends of starch with other polysaccharides, such as pectin, perform better with regard to hydration and have more favorable mechanical and thermal properties than the polymers alone [185,186]. Pectin is a non-toxic complex heteropolysaccharide with a linear backbone of  $\alpha$  (1–4) linked polygalacturonic acid residues and neutral side chain sugars [187]. The galacturonic acid can be partially methoxylated or amidated. Unmodified starch/pectin

blends can form films with mechanical properties like synthetic polymer films. Coffin & Fishman [188] reported that the mechanical properties of hydrocolloid films prepared with a starch/pectin ratio of 70/30 and glycerol as plasticizer are adequate for use as an edible biodegradable film. The hydrogen bond interactions of starch/pectin favor slippage of the pectin chains when stretched.

Sabando and Castaño et al. [189] reported novel hydrocolloid pectin-starch (30/70) films with bioactive extracts made from cross-linking pectin-starch gels with Poly(ethylene glycol) diglycidyl ether (PEGDGE). The films had the adequate water-uptake capability, ranging from 100% to 160%. PEGDGE also inhibits the disintegration of the pectin-starch films. Carreño and Castaño et al. [190] have reported a novel method for preparing green hydrogels synthesized by crosslinking polyvinyl alcohol (PVA) and aliphatic dicarboxylic acids. The hydrogels they produced had a specific release profile intended to carry active compounds or fillers for bioplastics and could be used for active food packaging.

#### 3.3. TPS Blends with Synthetic Polymers

The development of materials based on TPS with other synthetic polymers contributes not only to an increase in the performance properties of starch-based materials but also as a way to reuse plastic waste and to achieve higher quality products. Another advantage of the TPS/ synthetic polymer blends is that they are considered according to definition in ASTM D6852 bio-based materials [191]. A biobased product can be partially or fully made from renewable resources and the biobased content can be determined via ASTM D6866. Table 4 summarizes the main blend systems of starch-synthetic polymers and their characteristics.

## 3.3.1. TPS/Polypropylene (PP)

Polypropylene (PP) is a linear hydrocarbon polymer and is considered the secondmost widely used polyolefin produced and an excellent candidate for preparing TPS blends. However, PP and TPS are incompatible due to their differences in chemical structure: strongly polar for TPS and nonpolar for PP and hence the use of a compatibilizer, such as maleic anhydride grafted polypropylene (MA-g-PP), is common in TPS blends to improve the interfacial adhesion of the composite phases [192]. The maleic anhydride functional group, which is grafted into PP (PP-g-MA), forms covalent bonds with the hydrophilic starch being the most acceptable and economical compatibilizer for PP/TPS blends. Raee et al. [193] examined the influence of the maleic anhydride as compatibilizer and their concentration (up to 30%) on properties of PP/TPS blend. The results shown the rheological behavior, morphology, and mechanical properties were improved by increasing the amount of compatibilizer up to 20 wt%. Martins et al. [194] prepared PP/TPS blend with C14, C16 and C18 carboxylic acids as compatibilizers. Results concluded that the addition of carboxylic acids proved to be equivalent or better compatibilizers when compared to maleic anhydride polypropylene and no compatibilizer. In addition, the adhesion between both polymers phases was improved and the tensile strength, elongation and impact strength increased by the addition of carboxylic acids.

## 3.3.2. TPS/Natural Rubber (NR)

Rubbers are polymers that consist of organic compounds. Many types of rubbers exist such as Indian Rubber, latex, Amazonian Rubber, caucho, etc. The development of TPS films by including natural, modified or ozidized rubbers have interesting behavior. In some cases, the addition of rubber improves the tensile strength, however in other cases it results in a soft material [170,172]. It is important to mention that this is the function of the level of glycerol included in the TPS. On the other hand, reports by some authors [170,174,175] explain that a drastic increase in rubber level causes the separation of phases or agglomeration in the mix, resulting in a total change of matrix of materials. The blends became brittle with an irregular aspect and regions bearing free of rubber. As a consequence, the mechanical properties and water uptake of the material are unexpected,

showing dispersion in the obtained data. For this reason, low rubber content is desirable in many cases, in addition to the blends exhibiting high biodegradability [172]. It is worth mentioning that based on the results reported in literature, an optimal level of rubber can be added to the new blend of formulations to form continuous phases contributing to the resistance of the material with reach fractures or agglomeration. A better interaction with another kind of rubber gives differences in mechanical properties to those of others. For example, Cai et al. [172] reported better interaction of epoxidized rubber compared with natural rubber. These results are in line with those reported by Jantanasakulwong et al. [173], who proved the interaction of chitosan and starch with epoxidized natural rubber. They found that the chemical interaction of chitosan with the epoxy groups of the rubber exists and this interaction improved the mechanical properties of the blend. Saetun et al. [174] reported that the hydroxyl groups in the three-dimensional network of lignin in the rubber wood sawdust that could interact with starch to act as an interfacial compatibilizing agent and produce a higher tensile strength. Then, the molecular interactions and crosslinking of rubbers with starch or polymers resulted in changes in the mechanical properties of the films.

## 3.3.3. TPS/Polyethylene (PE)

Polyethylene is the most chemically simple polymer with a lineal chain backbone. It is obtained by the ethylene polymerization. Commercially, there are variations of polyethylene with different densities: low (PLD) and high (PHD). The PHD is characterized by possessing a great rigidity and resistance. Some advantages of the use of PLD are greater flexibility, good resistance to impact, as well as the high resistance at high temperature that this material possesses. The results shown by Arvanitoyanni et al. [178] found that LDP and rice starch presented low compatibility, which was difficult to modulate due to the tensile strength as the crystalline and amorphous regions were presented.

## 3.4. Starch Based Composite Materials

The incorporation of inorganic and organic reinforcements into a starch matrix allows us to obtain better mechanical and functional properties (Table 5). These reinforcements are added in low concentrations to the biopolymer matrix. The main challenges in preparing nanocomposites include achieving a high level of dispersion, finding suitable plasticizers, and controlling the interfacial strength of the inorganic reinforcement in the biopolymer matrix [93]. Thus, organic cationic compatibilizers have been used to improve the dispersion of clays in PTS [195].

Table 5. Composite system, processing techniques and main results of starch based materials.

Composite System	Starch Source	Compatibilizante	Processing Techniques	Conclusions	Reference
Starch/titanium dioxide (TiO <sub>2</sub> )	Wheat	Glycerol/maleic anhydride (MA)	Solution casting-Melt mixing	Is described as a reliable, reproducible, two-step preparation of highly homogeneous TPS/mTiO <sub>2</sub> composites, with very good dispersion of the filler.	[196]
Dialdehyde starch/magnetic nanoparticles	Potato	Maleic anhydride (MA)	Microwave-assisted in-situ precipitation method	The composite films manifested lower water vapor transmission, thus it can be concluded that MNPs improve the hydrophobicity and mechanical properties of MNPs/DAS composite films.	[182]
Starch/nanodiamond	Corn	Glycerol	Solution-blending.	The incorporation of a small amount of ND, the mechanical properties of starch were improved. To further improve the thermal stability and barrier properties of starch for food packaging applications	[197]

Composite System	Starch Source	Compatibilizante	Processing Techniques	Conclusions	Reference
PBAT/starch/clay	Tapioca	Maleic anhydride (MA)	Reactive extrusion	Grafting with MA also improves the mechanical properties, and nanocomposite can be exploited for various commercial packaging applications.	[152]
TPS/PP/HDPE/ nanoclaycorn	Corn	Glycerol/maleic anhydride grafted	Single-screw extruder	The addition of nano-clay to the system decreased the melt flow index, this may be due to the reaction between the modifying agent of the clay and Maleic anhydride being presented in PE-g-MA or/and the hydroxide in the glycerol.	[198]
TPS/PP/halloysite nanotubes	Corn	PP-g-MA	Internal mixer	The aforementioned results indicated that blending PP with TPS would successfully overcome the drawbacks of TPS such as poor mechanical properties and moisture sensitivity; in addition to improving the biodegradability of PP which is a real hazard for the environment. HNT could improve mechanical and thermal properties of the samples showing its usefulness as a promising filler	[193]
TPS/PP/date palm flour	Potato	PE-g-MA, 2% <i>w/w</i>	Extrusion	This indicates that in addition to the interactions existing formerly between the DPF flour and the TPS phase, esterification treatment improved also the wettability of the filler by the PP phase through mediating its hydrophilic character	[199]

## Table 5. Cont.

Inorganic reinforcements into starch-based composites for food application include clays (montmorillonite) (MMT) and bentonite [200], nano-clay [198,201], nano-silica (SiO<sub>2</sub>) [202], metal oxides [203].

Recently, Sarkar et al. [204] reported that bentonite and hectorite clay incorporation in starch-based nanocomposite incorporation strengthens the polymeric structure and increases the compatibility of starch/PVA blends.

Nano-SiO<sub>2</sub> is also a suitable nano-filler for TPS-based composite. The addition of nano-SiO<sub>2</sub> to TPS films exhibited better TS and Young's modulus [205]. Islam et al. [206] reported that the addition of clay to potato starch/hectorite nanocomposite films significantly improved their mechanical and biodegradability properties. Corn starch/clay films had the highest absorption and best antibacterial properties [207]. However, their swelling ratio increased with time, however decreased with the addition of plasticizer and hectorite clay. Solution casting of corn starch-lithium perchlorate (LiClO<sub>4</sub>)-nano-silica composites were prepared by Teoh et al. [208]. The network structure formed by combining nano-silica with corn starch prevented the water molecules from dissolving, improved the water resistance of the film, making nanocomposites a suitable candidate for packaging applications. Likewise, the incorporation of a natural and innocuous mineral filler, such as talc in films based on thermoplastic starch, allowed us to obtain a bionanocomposite suitable for food packaging with improved functional properties such as low water vapor and oxygen permeability [209].

## 3.5. Starch-Based Materials with Filler/Reinforcement

The incorporation of organic lignocellulosic fibers has been one of the main studied reinforcements to improve TPS properties. Many lignocellulosic fibers have been evaluated, including hemp, sisal, green coconut, cellulose fibers, nanofibers, and microfibers from recycled paper, polysaccharide-based nanocrystals, and microcrystalline cellulose [81,210–212]. Ochoa-Yepes et al. [213] investigated the effect of the incorporation of lentil flour fiber in thermoplastic starch films prepared by film casting. The composites containing lentil flour as filler demonstrated this fiber act as starch-glycerol film reinforcement, making them more resistant and protecting food products from being damaged. Similar results were previously reported by Glenn et al. [214] when preparing starch-based foam composites by extrusion foaming using different sources of cellulosic fiber: cellulose; softwood and hardwood pulp fiber; and municipal solid waste fiber. Increased tensile strength and tensile modulus without affecting the foam density were obtained in food packaging trays. Menzel [210] prepared starch-based films filled with cellulose fibers, and results showed that the cellulose fibers improved the resistance showing high-stress values (1086 MPa). They attribute this behavior to starch-cellulose interactions, which decrease starch chain mobility [215]. Most research papers reported that the addition of fibers among 2.5–3.0% of fibers improved the mechanical resistance of films [210,211,216], although a fragile structure is also presented. This is attributable to the nonhomogeneous structure of films, resulting in brittle composites.

The processing method and length of fibers added to a film's formulations have an important effect on the mechanical properties. Then, some processing techniques involving compression, molding, or mechanical processing could impact fiber length and a film's final fiber content. As a result, the mechanical properties of the final products are affected. Liu et al. [217] prepared biocomposite from kenaf fiber and soy-based bioplastic with extrusion injection molding, compression molding, and injection molding. The results suggested that compression molding processing is beneficial to both the thermal and mechanical properties of the composites. Compared with the synthetic materials (e.g., low-density polyethylene), some films' reinforcement with fibers or nanofibers exhibit less tensile strength (0.24–0.50 MPa). This can be positive in terms of the biodegradability of materials. For meat packaging development for specific food applications, other physicochemical characteristics in films must be analyzed with caution, e.g., water vapor permeability.

#### 4. Advance in Preparation of Functional Starch-Based Food Packaging

Recent advances in the development of starch-based materials for food packaging applications are based on the combination of the emergence of new preparation techniques, equipment and the manipulation of matter at the nanometer scale, which have allowed us to achieve special properties with adequate performance [218,219].

## 4.1. Incorporating Bioactive

In recent years the incorporation of additives such as antioxidants and antimicrobials in starch-based films plays a key role in improving functional properties. These active packaging films provide a semi-permeable barrier that helps to extend shelf life by reducing the migration of moisture, loss of solutes from fruit respiration and oxidation reaction [218,220]. Essential oils are a clear example of active components in food packaging, their antioxidant and antimicrobial properties have improved the quality and safety of food [221]. Essential oils are natural substances composed of alcohols, phenols, terpenes, esters and among other bioactive agents, whose main function is the release of their active components avoiding microbial and fungal attack and oxidation of food [218]. Oregano oil, thyme [38], cinnamon bark, clove [222], ho wood (Cinnamomum camphora), and cardamom [223] have been evaluated as additives in the control of various pathogens.

Raigong et al. [224] evaluated the addition of clove oil and cinnamon oil in starch films against *S. aureus*, *C jejuni* and *E. coli*, and the results showed the inhibition of the pathogens. Clove oil inhibited between 22–100%, while cinnamon oil was effective against *C. jejuni* (19–22% inhibition) and *E. coli* (33–40% inhibition), respectively. Souza et al. [223] evaluated that the addition of Pickering emulsions to essential oils, ho wood (Cinnamomum camphora), cardamom, and cinnamon, showed that the ho wood oil lowered water vapor transmission rate, improving the release of the active compound. Ho wood oil was the most promising with regard to being applied as a biodegradable active packaging. The addition of natural extracts from various sources, such as fruit by-products, has been evaluated in starch-based films. Mango puree and pineapple pomace were incorporated into maize starch-gelatin films, improving the physicochemical properties of the films and increasing the antioxidant activity and antimicrobial activity [218]. Table 6 lists the most recent studies on starch-based bioactive systems prepared by film casting method for food packaging applications.

System	Starch Source	Bioactive	Results	Application	Reference
Poly (vinyl alcohol)-corn starch	Corn	Pineapple peel extract as a natural antioxidant agent	Film thickness and water vapor permeability increased slightly, antioxidant capacity increased.	Food Packaging	[225]
Lemon essential oil/surfactants (Span 80, Tween 80)/corn and wheat starch	Corn and wheat	Lemon essential oil	All concentrations of lemon oil were effective against selected bacteria (both Gram-negative and Gram-positive) compared with control film (without lemon oil)	Food Packaging	[226]
Chitosan-Starch-antioxidants	Rice	Antioxidants (from cranberry, blueberry, beetroot, pomegranate, oregano, pitaya and resveratrol, thymol and carvacrol)	The addition of natural extracts gives chitosan-starch a higher apparent density values. The addition of natural extracts provided chitosan-starch films with better thermal and physical properties	Food Packaging	[227]
Sodium alginate-starch	Үисса	Anthocyanin and betanin (from the exocarp of the black eggplant (Solanum melongena) and the mesocarp of beet (Beta vulgaris))	Incorporation of natural extracts influenced the mechanical properties, however did not influence film thickness or water vapor permeability. Films with eggplant extract had higher antioxidant activity against the (DPPH) radical and were more sensitive to the exposure of gaseous amines in comparison with films with beet extract	Food Packaging	[228]
Mung bean starch-chitosan (MSC) Water chestnut starch-chitosan (WSC)	Mung bean/Water chestnut	Hydrophobic perilla oil	The results showed that the cheese coated by WSC film containing perilla oil presented better treatment performance in terms of microbial growth delay, weight loss and shelf life length.	Food Packaging for cheese	[229]
Cassava starch- essential oil-sodium bentonite nanclay	Cassava	Cinnamon essential oil	The meatballs stored at ambient temperature in cassava starch film incorporated with cinnamon oil and nano-clay, significantly inhibited the microbial growth till 96 h below the FDA limits (106 CFU/g) in foods compared to control films that exceeded the limit within 48 h.	Food Packaging for meatballs	[230]

**Table 6.** Bioactive system, processing techniques and main results of bioactive starch based materials for food applications.

Table 6. Cont.

System	Starch Source	Bioactive	Results	Application	Reference
Starch-furcellaran-lavender essential oil-gelatin	Potato	Lavender essential oil	Antioxidant properties proved to be significantly enhanced with increasing lavender essential oil concentration. The solubility, water absorption and degree of swelling of the film decreased with increasing concentration of oils.	Food Packaging	[231]
Tapioca starch-cinnamon bark essential oil-glycerol	Таріоса	Cinnamon bark essential oil	Increasing cinnamon bark essential oil improves tensile strength and antibacterial activity of the film and preserved the freshness of the beef during 15 days of storage.	Food Packaging for fresh beef	[232]
(Gelatin-pectin-starch)- (gelatin-pectin)-(gelatin- starch)-(starch-pectin)	Potato	Mentha pulegium and Lavandula angustifolia essential oils	The incorporation of essential oils resulted in films with enhanced antibacterial properties, lower water vapor permeability, and reduced mechanical properties	Food Packaging	[233]
Carvacrol essential oil-corn starch-montmorillonite- tween 80/Carvacrol essential oil-glycerol-corn starch	Corn	Carvacrol essential oil	The starch-montmorillonite-carvacrol essential oil hybrid films showed antimicrobial behavior against <i>E. coli</i> .	Food Packaging	[234]
Arrowroot starch-carnauba wax nanoemulsion-cellulose nanocrystals-essential oils from Mentha spicata and Cymbopogon martinii	Arrowroot	Mentha spicata and Cymbopogon martinii	The essential oils from Mentha spicata and Cymbopogon martinii incorporation improved the thermal stability of the films and provided excellent protection against fungi Rhizopus stolonifer and Botrytis cinerea. The addition of thuma essential oil	Food Packaging	[235]
Corn starch-thyme essential oil microcapsules	Corn	Thyme	microcapsules to starch films increased the opacity, thickness, tensile strength and water solubility. They also showed an inhibitory effect against Botryodiplodia theobromae Pat and Colletotrichum gloeosporioides Penz and extended the shelf life of mangoes up to 10 days at 25 °C.	Food Packaging for mango	[236]
Corn starch-PVA- neem and oregano essential oils	Pea	Neem and oregano	Starch-PVA films with 6.7% of oregano essential oils exhibited the best physical properties, without significant differences with respect to the starch-PVA matrix, while exhibiting antibacterial activity.	Food Packaging	[237]

## 4.2. Starch Nanostructures (SNEs)

The field of natural biopolymers have shown great potential for important, rapidly growing applications ranging from green electronics, food packaging, dye and heavy metal removal, oil/water separation, therapeutic agent delivery, tissue engineering scaffolds, biological devices, optics, and sensing [238]. However, the application of advanced functional biopolymer materials suffers from their poor processability and weak mechanical properties. Regarding this, there are enormous challenges to break the strong intermolecular interactions (hydrogen bonding) in their native forms, while re-establishing predominant hydrogen bonding in the processed materials in a cost-effective way. The introduction of one or more new functional groups into native polysaccharides alters their physical, chemical and, above all, biological properties. The biological properties of polysaccharide derivatives depend on the molecular weight, the type of modification, the type of native polysaccharide, the conditions of the modification process, the solubility and the conformation of the polysaccharide. The manipulation of matter at the nanometer scale (1 to 100 nm) has recently been studied to create new materials and devices with special properties and adequate performance. The unique properties of nanoparticles depend on the size and shape, charge and surface modification, and hydrophobicity of the starting material [239]. For example, starch nanoparticles prepared by acid hydrolysis from waxy corn and high amylose maize starch exhibit a crystal structure and size of type A-type, B-Type, and 50 nm, 540 nm, respectively, while their morphology was polygonal and smaller starch granules, pores, respectively [240].

In order to alter the crystalline structure of the starch, SNEs are obtained mainly by top-down and bottom-up methods. In the "top-down" method, macroscopic materials are reduced from the microscale to the nanoscale through physicochemical processes such as acid hydrolysis [105,241] due to the sensitivity of the amorphous rings in starch granules to acid treatment, homogenization [69], crushing [242,243], gamma irradiation [244], and ultrasound [245,246]. Acid hydrolysis and ultrasonication methods are particularly effective in breaking up the aggregates of nanoparticles formed through hydrogen bonds, thereby reducing the size and polydispersity of nanoparticles [247].

In the "bottom-up" process, SNEs can be obtained from a buildup of starch molecules in a controlled manner that is regulated by thermodynamic means such as regeneration [248] nanoprecipitation or self-assembly [242]. Micro-nano emulsion and nanoprecipitation are very simple and convenient methods for producing nanoparticles with a desired size [249]. For example, starch granules are dispersed in water or dimethylform sulfoxide, completely gelatinized at 100 °C, and then precipitated by dropwise addition of nonsolvents (such as methanol, ethanol, isopropanol, n-propanol) to obtain SNPs with different sizes [250,251]. In addition, it has been shown that the combination between chemical methods, for example acid hydrolysis, and physical methods such as ultrasonication, generates higher homogeneity and yield in the obtained starch nanostructures [248,252,253].

Among the recently studied starch-based nanostructures are nanoparticles [254,255], nanospheres [18,256], nanocrystals [253,257,258], nanomicelles [259,260], nanogels [261] and nanofibers [262]. Table 7 summarizes the main preparation methods and size of starch nanostructures. Emphasis is placed on their responsiveness, permeability, toxicity, interactions with other components and applications. The aim of producing such nanocrystals or nanoparticles is to use them as fillers in polymeric matrices to improve their mechanical and/or barrier properties. Starch nanoparticles are non-toxic and respond to pH, temperature, light and other stimuli. Starch nanoparticles have a wide range of applications, such as improving the mechanical properties of films and gels, stabilizing emulsions, use as a fluorescent indicator, forming or directing agent in self-assembling structures, scaffolds, and reconstruction of hollow organs.

Nanoestructure	<b>Raw Materials</b>	Preparation Method	Size (nm)	Reference
Nanocrystal	Potato	Acid hydrolysis-ultrasonication	40-70	[151]
Nanocrystal	Pea	Acid hydrolysis-ultrasonication	30-80	[253]
Nanocrystal	Waxy	Acid hydrolysis-ultrasonication	70-100	[66]
Nanocrystal	High amylose maize	Acid hydrolysis	118-130	[18]
Nanospheres	Soluble starch	Micro-emulsion	50-350	[263]
Nanospheres	Native sago starch	Nanoprecipitation	270-420	[256]
Nanospheres	Corn	Microemulsion	96-100	[264]
Nanospheres	Corn	Nanoprecipitation	90-100	[265]
Nanospheres	Potato	Acid hydrolysis-ultrasonication	40	[266]
Nanogels	Corn, potato, and pea starch	Reverse emulsification	100	[267]
Nanogels	α-starch	Chemical crosslinking	30	[261]
Nanogels	Starch/poly(alginic acid-cl-acrylamide)	Chemical crosslinking	380	[268]
Nanogels	CMS	EB radiation N	380	[269]
Nanogels	Potato	Chemical crosslinking	120-160	[270]
Nanofibers	Corn	Electrospinning	750-900	[271]
Nanofibers	High amylose Maize starch	Cross-linking/Electrospinning	300–700	[272]
Nanofibers	Corn	Coaxial Electrospinning	110-160	[273]
Nanofibers	High-amylose maize starch and nGO	Electrospinning	30–50	[274]
Nanofibers	Soluble starch	Coaxial electrospinning	90-250	[262]
Micelle	Corn	Graft copolymerization/self-assemble	20-30	[275]
Micelle	Waxy Maize	Emulsion/self-assemble	60-70	[276]
Micelle	Soluble	Schiff-base bonds		[277]
Micelle	Starch-octanoic	Graft copolymerization/self-assemble	400-600	[278]
Nanoparticulas	Waxy Maize	Acid hydrolysis-ultrasonication	50-80	[252]
Nanoparticulas	Waxy Maize	Enzymatically hydrolyzed-emulsion cross-linking	80–130	[248]
Nanoparticulas	Pea	Precipitation-complex formation	50-100	[254]
Nanoparticulas	Corn	Complex formation	10-20	[248]

Table 7. Preparation methods and size of starch nanostructures.

#### 5. Processing Techniques

## 5.1. Traditional Techniques

5.1.1. Extrusion

When you think of food packaging based on starch or polymer blends with starch, extrusion is one of the most used processes for their production. The extrusion process consists of subjecting the starch to relatively high pressure, heat and shear forces that produce multiple chemical and physical reactions, which decrease its crystallinity [279]. This process can be of three forms: extrusion blowing, compression extrusion molding and extrusion injection molding [280]. In extrusion, in addition to gelatinization, starch degradation occurs due to the partial depolymerization of amylose and amylopectin, the latter being the most affected by its rigid structure [281]. During processing, the molecular weight of amylopectin decreases by a factor of 15, while for amylose it decreases only 1.5 times [282]. Processing parameters such as temperature, residence time, water content, plasticizer type and percentage, temperature, shear stress, and shear speed influence the final properties of TPS [283].

The extrusion process has excellent mixing capacity, is continuous, efficient, lowcost, and highly flexible in operation, thus enabling large-scale film production [279]. In addition, controlling the humidity properly during the process would affect the viscosity and the efficiency of the extrusion, increasing the inhibition of retrogradation of the film and therefore its mechanical properties [284]. The chemical composition, crystal structure and morphology of the starch granules also influence the final properties of TPS. High amylose starches are preferred for film production as they are resistant and more flexible [285] For example, Rindlav-Wrestling et al. [286] studied the mechanical and barrier properties of TPS films obtained from "high amylose" and "waxy" potato starch. The authors concluded that tensile strength, barrier, and water permeability properties were better in high amylose TPS films. Thuwall et al. [15] evaluated the effect of amylose content in obtaining TPS. The TPS obtained with "high amylose" potato starch during extrusion exhibited unstable flow and nozzle clogging, however, they showed better mechanical properties such as tensile strength and elongation at break than the starch extruded TPS "normal". Pure starch does not meet the properties necessary for the manufacture of films, so it is necessary to mix it with a plasticizer or another polymer. Table 3 shows some blends of starch with different polymers such as polylactic acid (PLA), polybutylene adipate-terephthalate (PBAT), polyvinyl alcohol (PVOH), chitosan and polycaprolactone (PCL) that have been processed by extrusion to improve their performance in film formation. Yusoff et al. [62] made a bioplastic of tapioca starch (TS) with PLA (10–50 wt%) and determined that the tensile strength improved by 26% and the impact testing value decreased with the addition of 30% of TS as extrusion reduced the retrodegradation of the starch. Likewise, Hubackova et al. [164] evaluated the biodegradable capacity of an extruded mixture of corn starch with PLC and determined that the mixtures with starch plasticized with glycerol had better mechanical properties and a higher degree of biodegradability in an aerobic environment. This was due to the extrusion improving the incorporation of the mixture and the disposition of the polymer chains in relation to the environment to be degraded.

Extrusion has not only favored the development of polymeric starch mixtures, but its mixing efficiency has also allowed the development of nanostructured materials with nanofibers, nanoparticles and high-value compounds to develop smart packaging. For example, Zhou et al. [287] made antimicrobial films of a starch-PBAT mixture with AgNPs@SiO<sub>2</sub> nanoparticles by extrusion and found that the films had good mechanical properties and increased the hydrophobicity of the surface compared to films without particles. Additionally, the films were tested to pack peaches and nectarines at 53% relative humidity and 24 °C and were found to inhibit microbial spoilage and extend shelf life. On the other hand, Ceballos et al. [288] developed an extruded film of starch with yerba mate extract and found that at a concentration of 20% the yerba mate extract behaved as a plasticizer, since the deformation at break and the toughness increased considerably. Also, they determined that the films disintegrate after 10 weeks of burial, and therefore serve as a great example of biodegradable material.

## 5.1.2. Foaming Processing

The foaming process of a polymer is a thermodynamic process composed of cell nucleation, growth of the structure and thermal stabilization. Nucleation is initiated by thermodynamic instability in a polymer saturated with gas at high temperature and pressure [289]. The foaming process of a polymer can be carried out by extrusion, thermopressing, microwave heating, solvent extraction, and supercritical fluid extrusion [290]. The most commercialized foamed packages are those of expanded polystyrene due to their high resistance, low density and low cost. However, these are not very friendly to the environment, since they could take a long time to degrade [291,292]. Therefore, it is necessary to develop foams from biodegradable materials such as starch. The low mechanical resistance, high hydrophilicity, low resistance to retrogradation and low thermal stability posed by starch make it a material not suitable for being foamed [290]. That is why blends of starch with polymers and plasticizers have been used to improve the mechanical properties of the resulting foams (Table 3). Chauvet et al. [293] developed a biodegradable foamed material with PLA and TPS using CO<sub>2</sub>-assisted supercritical extrusion (scCO<sub>2</sub>). In their study they determined that with the mixture of 80:20 PLA and TPS, respectively, a foam with a uniform structure was obtained and that the expansion and porosity of the mixture behaved as pure PLA with high porosity (96%). Likewise, Cheng, et al. [294] made foams by means of scCO<sub>2</sub> assisted extrusion of TPS with glyceraldehyde, and improved the expansion ratio, the resilience rate, the complex dynamic moisture-proof viscosity and the crystallization rate of the foam by additional integration of crosslinking agents such as

sodium hexametaphosphate and nano-silica particles. On the other hand, Zabihi et al. [295] made foams with a mixture of thermoplastic corn starch (TPS) and polystyrene (PS) by melt extrusion and used glycerol and water as plasticizer. They determined that the addition of 20% PS to TPS caused an expansion of the foams six times higher than that of PS and 60% higher than that of TPS, while the moisture absorption was 50% less than that of TPS.

## 5.1.3. Film Casting

The film casting method is the most used for the manufacture of biodegradable films. This consists of a solution prepared by the stirring and heating of the film-forming polymers and the solvent, and subsequently the solution is degassed, poured onto a flat and balanced surface [296]. The drying of the film can be at room temperature or in an oven with controlled temperature and humidity conditions. The advantages of this method are the practicality and low cost, while disadvantages are that it is difficult to control the thickness and uniformity of the film, and therefore the quality [296]. Due to the limitations of the method, it is difficult to use it for large-scale film production, which is why it is seldom used in the industry. To make films by the film casting method, polymeric blends, acidifications and simple and double modifications of native starches have been made to obtain materials with the appropriate characteristics (Table 3). For example, Pavoni et al. [163] evaluated the effect of adding lactic or acetic acid to the film-forming solution based on cornstarch and chitosan. They found that the samples acidified with acetic acid presented higher stiffness, less deformation, higher values of Young's modulus and lower percentage of elongation compared to those acidified with lactic acid. These films also had better water vapor barrier properties and began degradation after 15 days. Cheng et al. [297] made packaging films with cassava starch (native and doubly modified) and red cabbage extracts using the casting technique. They determined that the doubly modified cassava starch films had better transparency, water resistance, water vapor barrier capacity, and tensile strength than native cassava starch films. In addition, they determined that anionic cassava starch formed stable complexes with anthocyanins through electrostatic interactions and hydrogen bonding, improving the physical and chemical properties of the films. For their part, Macêdo et al. [296] made a bioplastic of native and modified green banana starch, and determined that the modification of the starch increased the mechanical properties reaching a modulus of elasticity of 12.38 MPa, a tensile strength of 27.09 MPa, an elongation of 6.0%, a resistance to perforation of 251.8 N and a deformation of 2.8 mm.

## 5.2. Emerging Technologies

The demand for materials with characteristics superior to reinforced and functionalized materials has led to the development of new technologies for the processing of materials such as electrospinning, forcespinning, 3D-printing and reactive extrusion. These manufacturing processes provide materials with structural, material distribution in space, chemical, physical and biological differential characteristics. These polymeric modifications allow us to obtain materials with memory, with the capacity to generate and store energy and regenerate tissues, so these processes give way to the manufacture of thirdgeneration materials.

#### 5.2.1. Electrospinning

Electrospinning is not a recently created process, however, in the 1990s it was taken up and perfected by Reneker et al. [298], which is why it is considered an emerging process for the manufacture of fibers. Electrospinning is made up of two different processes: electrospray and spinning. Typical equipment configuration includes a solution tank with rows, a grounded collector, and high voltage power supply [299]. In this device the polymeric solution is pumped towards the tip of the collector that acts as an electrode and a high voltage between 100 to 500 kV/m is applied. The polymer solution will experience electrostatic forces due to the repulsion between the surface charges of the polymer and coulombic forces due to the external electric field [300]. This electrodynamic process causes the droplet to accelerate and experience jet bending instability to form the Taylor cone. The droplet is then split into micro or nanofibers in the grounded collector [299]. Starch has great potential when it comes to producing nanofibers by electrospinning and it has been shown that it can be electrospun mixed with other polymers, for example: Sutjarittangtham et al. [299] elaborated natural tapioca starch fibers using a collecting bath with ethanol at -20 °C and obtained fibers of 1.3 to 14.5  $\mu$ m in diameter from simple solutions of starch at 3 and 5% concentration, respectively. By X-ray diffraction (XRD) it was determined that electrospinning did not modify the crystalline structure of starch. Likewise, Fonseca et al. [301] elaborated electrospun fibers of native and anionic (phosphorylated) corn starch with high and low amylose content and determined that the fibers obtained from starch with high amylose content had a homogeneous morphology unlike of the regular starches that presented binders attached to the fibers and a heterogeneous structure. Therefore, they concluded that a higher amylose content of starches favors electrospinning. For their part, Cárdenas et al. [302] compared starch fibers obtained by electrospinning of native, commercial and cationic potato starch. Through their study they confirmed that the fibers were cationized with a highly amorphous state and that they had a heat resistance of 300 °C due to the physicochemical changes generated in the fibers.

## 5.2.2. Forcespinning

Forcespinning is a novel method for the large-scale production of polymeric fibers, reaching diameters from 50 nm to 1000 nm. This method uses centrifugal force, which allows for a significant increase in output throughput and nanofiber production [303]. The forcespinning machine is composed of a spinneret, into which the polymeric solution is injected. This spinneret has a needle that, when rotating at high speed, prints the fibers on a crown. The crown is composed of 16 needles distributed 30 cm from the needle and the fibers are collected with a metal frame  $(1 \times 1 \text{ in})$ . The spinning machine can operate at an angular speed of 3000 to 7000 rpm [304]. The viscosity of the polymer solution and the evaporation characteristics of the solvent are important parameters for forcespinning. Starch is a suitable polymer to spin by forcespinning, since Li et al. [305] manufactured fibers with native corn and potato starches rich in amylopectin (65%). They determined that the concentration of the crosslinking agents in the solution to be spun was crucial for obtaining the fibers. The morphology of the maize starch fibers was homogeneous, while that of potato was heterogeneous with the presence of binders. Regarding the diameter of the fibers obtained, it was 1.3  $\pm$  0.4 and 1.5  $\pm$  0.6  $\mu$ m for the fibers of corn starch and potato, respectively. Li et al. [306] also manufactured fibers by forcespinning blends of potato starch with polyethylene oxide (PEO) to encapsulate drugs such as ibuprofen and ketoprofen. The diameters of the nanofibers were 2.6  $\mu$ m and presented a uniform morphology. These nanofibers worked well to encapsulate drugs, so starch has the potential to encapsulate antimicrobial compounds in food packaging.

## 5.2.3. 3D-Printing

3D printing is a technology that allows rapid prototyping through a 3D printer, adding layer-by-layer materials based on reconstructed models using computer codes [307]. The World Economic Forum considers 3D printing as "the third industrial revolution". 3D printing has developed rapidly and has been applied in many industries, such as medicine, aerospace, automotive, food, art, textile, architecture, etc. However, there is a huge gap in the application of 3D printing for the manufacture of food packaging, since there are few developments, for example, Leaw et al. [308] developed printed edible corn starch and gelatin films by 3D. In addition, they evaluated the concentration of glycerol and hawthorn berry extract on the texture of the printed films. They determined that the 4% glycerol film had the highest elongation at break of 71.57% and showed inhibition against *Pseudomonas aeruginosa*, suggesting that they can be used for antibacterial food packaging. For all the above, it can be said that there is a lot to do in terms of 3D printing of edible films,

antibacterial, antioxidant, enzyme inhibitor, deodorizer, coatings with color and aroma for fruits etc.

#### 5.2.4. Reactive Extrusion

In the reactive extrusion process, the extruder is used as a chemical reactor, which makes it possible to unify the polymerization and/or modification process of the polymer and the granulation process in a single stage [309]. This procedure is generally carried out in co-rotating twin screw extruders, due to its high mixing capacity and continuous operation [152]. The great advantage of this extrusion is that the polymerization reactions are carried out in the absence of solvents or using a minimal amount of them. This process is generally used for rapid reactions of 1 to 15 min, such as crosslinking, glycolysis, hydrolysis, compatibilization, etc. For example, Nayak [152] used reactive extrusion to make composites of tapioca starch, polybutylene adipate terephthalate (PBAT), and nanoclay. Through mechanical tests, it was determined that the tensile modulus and elongation at break increased with the incorporation of 30% TPS and 44.45% nanoclay. Gutiérrez and Valencia [309], phosphated corn starch by reactive extrusion using sodium tripolyphosphate as a cross-linking agent. However, they determined that phosphating did not favor the physicochemical properties of the manufactured materials with respect to the TPS control film. For their part, Bai et al. [310] compatibilized thermoplastic starch and PBAT by reactive extrusion using reactive epoxy compatibilizer (REC) for the manufacture of films. The results indicated that REC effectively improves the compatibility of the TPS/PBAT mixtures and extends the polymeric chains of PBAT by improving the mechanical properties of the films.

## 6. Starch Based Materials Application in Food Industry

A fundamental part in the food packaging industry is to innovate, develop new materials with improved properties, reduce food waste, and be economically viable and sustainable, while at the same time complying with the standards of quality, safety and functionality; contain, protect and conserve. Another important issue is that developed materials must facilitate product handling, although they must also preserve nutritional value. Currently, the use of bioplastics has increased significantly, and it is estimated that by 2022 the production of bioplastics will be around 2.44 million tons due to a great demand for biopolymers for various applications and product [5]. This increase in the manufacture of biopolymers as substitutes for conventional packaging is mainly due to the biodegradability, biocompatibility and low cost of these starch base materials [311] as starch by itself or in combination with other biopolymers, have been used in the preservation of fresh products.

One of the strategies to generate interest among consumers and for the packaging industry to commercialize starch-based materials have been the development of smart and/or functional materials to extend the shelf life of packaged foods (Figure 3). In this context, the main work has focused on: (i) improving the materials so they provide a better barrier to oxygen and water vapor materials by mixing different materials and incorporating micro/nano structures; and (ii) adding bioactive substances such as antioxidant or antibacterial agents by means of micro/nano encapsulation [280].



Figure 3. Active and smart starch-based food packaging to improve shelf life.

Active packaging deliberately modifies the product or environment to improve food safety and quality. Hence, increased attention has been paid to the preparation of bioactive and smart packaging films by active films having antibacterial, antioxidant, and barrier properties [312,313]. Other examples of active packaging include oxygen scavengers to decrease fat oxidation, ethylene scavengers to minimize fruit and vegetable ripening, humidity and odor absorbers [314–318].

Smart packaging informs the consumer about kinetic changes related to the quality of the food or the environment it contains, to minimize losses and ensure food quality. Hence, the temperature can be monitored, providing a thermal history of the foods storage, and informing the most suitable consumption conditions. Some studies have been carried out to produce such materials, and commercial packaging is available in the market. Jederman et al. [319] monitored the temperature curves allowing the evaluation of the cooling efficiency in bananas, the effect of changes in packaging and the respiration heat. Commercial brands are patented by MonitorMark<sup>TM</sup> and commercialized as a Time–Temperature Indicators (TTI) sensor developed by 3M<sup>TM</sup> (3M<sup>TM</sup>, Maplewood, MN, USA) and CoolVu indicator developed in Freshpoint-Switzerland.

Fish and meat products are highly susceptible to decomposition by oxidation of fats showing color changes, (e.g., discoloration of pigments such as myoglobin, carotenoids), and off-odors and flavors (e.g., rancidity as a result of lipid oxidation), which leads to nutrient losses (e.g., oxidation of vitamin E,  $\beta$ -carotene, ascorbic acid) and adversely affects the quality [320]. In order to prevent those problems, vacuum packaging has been used as this method does not always remove all oxygen under the packaging. That is why it has been necessary to develop novel packaging materials to prevent oxidation and meat quality loss. In this sense, oxygen scavengers have been supplied in packaging to eliminate the residual oxygen. The oxygen scavengers are incorporated in sachets, films or labels to prevent food products contamination or accidental consumption. Among the substances incorporated are iron powder, ascorbic acid, dyes, enzymes (glucose oxidase and alcohol oxidase), unsaturated fatty acids (oleic or linoleic acids), and immobilized yeast [217]. On the other hand, thermoplastic starch films have also been developed with the purpose of reducing lipid oxidation in foods. Panrong et al. [321] prepared thermoplastic starch films incorporating low-density polyethylene and green tea. They proved that the hydrophobicity of films allows a reduction in the lipid oxidation of packaged soybean oil, which was effectively reduced by up to 38% depending on the TPS ratio used. Similarly, Piñeros-Hernandez et al., [322] prepared edible cassava starch films carrying rosemary

antioxidant extracts for use as potential active food packaging. They reported the films enhanced the UV-blocking properties of the films. In this context, several works have been mentioned above in Section 4.1.

Smart packaging films based on a change of color have been developed, and they have pH-sensitive and responsive indicators (e.g., anthocyanins, betacyanins, and curcumin) in a biopolymer-based matrix [312]. These materials are usually synergistically blended with other polymers (PVA, PLA, carrageenan, chitosan), can also respond to magnetic field, or have enzyme-responsive characteristics [313]. Recently, the application of natural pigments and polymer carriers has shown great potential in smart packaging based on pHresponsive indicators [323]. A research work conducted by Silva-Pereira et al. [324] revealed the use of blueberry residues as a potential visual pH indicator in the monitoring of fish spoilage. The indicator carrier matrix was corn starch and chitosan and showed good pH sensitivity and thermal stability. Similarly, films based on cassava starch and anthocyanins showed high pH sensitivity over a wide pH range, which allows monitoring of the quality of various foods [325]. In addition, potato starch-based films with anthocyanins can successfully display the color difference at pH 1-12 and detect the fresh stage (pH = 5.8) and spoiled stage (pH = 8) of pork, demonstrating the potential of potato starch for food product quality detection [326]. Shapi'i et al. [327] evaluated the effect of incorporating chitosan nanoparticles into a starch matrix on the antibacterial properties of the film. The authors found that the starch/chitosan nanoparticle film used to package cherry tomatoes effectively inhibited the growth of microorganisms (7  $\times$  10<sup>2</sup> CFU/g) compared to pure starch film  $(2.15 \times 10^3 \text{ CFU/g})$ . Another way to inhibit the growth of microorganisms in starch films was reported by Diaz-Galindo et al. [328] by adding a cinnamon oil emulsion to the matrix that reduced the growth rate of Botrytis cinerea by 66%, preventing further contamination of the fruit during storage and transport.

The incorporation of anthocyanin-rich bay laurel berry extracts (BBE) into tapioca starch to develop food packaging films with antioxidant and pH-sensitive properties was studied by Yun et al. [329]. The work demonstrated a significant increase in the DPPH radical scavenging ability of the composite film  $(24.39-75.01\% \text{ under } 5 \text{ mg mL}^{-1})$  with the incorporation of BBE into the starch matrix. It was observed that when the starch-BBE film was exposed to hydrogen chloride, the color of the film changed from purple to red. The film quickly turned blue and then olive when exposed to ammonia gas. Jayakumar et al. [330] incorporated nutmeg oil, ZnO NP and ham extract into starch/PVA based films. These films showed pH sensitive and antibacterial properties. Under acidic pH, the dark purple extract turned cherry red, while at alkaline pH it changed to brownish yellow to light green at neutral pH. The film mixed with ZnO NP and nutmeg oil inhibited the growth of the foodborne pathogen Salmonella typhimurium. Similarly, the results of Mustafa et al. [331] demonstrated a variation in the coloration of smart and bioactive PVA/starch/propolis/procyanidin rosemary extract films depending on pH; reddish to blue under acidic pH, blue under neutral pH and yellow under alkaline pH. The maximum diameters of the film inhibition zone against *E. coli* and methicillin-resistant *S. aureus* were 21 and 15 mm, respectively. Table 8 summarizes some applications in the packaging of various foods, such as fruits and vegetables, bakery goods, meat, and starch-based materials indicating good prospects for commercial utilization.

Packaging System	Processing Techniques	Function	Food Application	Results	References
Rice starch in combination with chitosan, emulsifier (sodium caseinate), and red palm oil.	Dipping	Enhancing the shelf life of walnuts	To coat dried walnut kernels	Films with higher in elongation at break, but lower in tensile strength. Film is more flexible than the other corn and wheat starch films tested in this study. Rice starch with high flexibility produces a uniform layer on the surface of walnut.	[332]
Cassava starch at different concentrations (1%, 2%, 3% and 4%)	Dipping	Delay the ripening of papaya fruit ( <i>Carica papaya</i> )	Coating papaya fruit (Carica papaya)	All cassava starch coating concentrations reduced fruit maturation and anthracnose, with the 2%, 3% and 4% coatings giving 100% disease control.	[333]
Nano-SiO <sub>2</sub> -potato starch	Film	Preservation the white mushroom	White mushroom	The water resistance and mechanical properties of the films were improved with the addition of nano-SiO <sub>2</sub> . Resistance to ultraviolet and thermal aging was also improved. Finally, they were more efficient against <i>Escherichia coli</i> ( <i>E. coli</i> ) than <i>Staphylococcus aureus</i> ( <i>S. aureus</i> ), improving the preservation of white fungi.	[334]
Corn starch (TPS) and chitosan oligomers	Film	Package perishable foods such as strawberries, ricotta, and flavored breads,	Strawberries, ricotta, and flavored breads.	Sachet type packages demonstrated to have a notable antimicrobial capability against molds and yeasts. Flavored breads were the least susceptible product to the microbial development, while strawberries and ricotta presented the highest molds and yeasts growth, respectively.	[335]
Yam starch-glycerol	Film	Extend storage life of strawberries stored at 4 °C and 85% RH	Strawberries	Yam Starch films significantly reduced decay of the fruits compared to control and extended the shelf life of strawberries by 21 days.	[336]

**Table 8.** Packaging system, food application and mains results of pre-commercial studies of starch based materials.

Thus, Oliveira et al. [333] evaluated different concentrations of cassava starch in the protection of papaya fruit, reducing the ripening of the fruit and controlling diseases by 100%. Castillo et al. [335] made a Sachet type package of corn starch and chitosan oligomers for perishable foods such as strawberries, ricotta, and flavored breads. Table 9 lists the starch-based products currently available and marketed for food packaging applications where Biotec, Novamont and BioBag Americas are the main manufacturing companies.

Table 9. Commercially available starch-based materials for food packaging applications.

Material	Product	Manufacturing Company	Web Site	
Granules based on corn powder/polyester + corn powder	Bio Degradable Bio One and Bio Base Rangdaneh Sirjan	RANGDANEH SIRJAN Co. Sirjan-IRAN	http://www.rangdaneh.ir (accessed on 20 November 2021)	
BIOTEC contains 75% renewable feedstock and has a 69% biobased carbon share according to ASTM D6866 and ISO 16620-2.	BIOPLAST 105 BIOPLAST 300 BIOPLAST 400 BIOPLAST 500 BIOPLAST 900 BIOPLAST GF 106/02 BIOPLAST GS 2189	BIOTEC GmbH and Co. KG Emmerich am Rhein-Alemania	https://es.biotec.de (accessed on 20 November 2021)	
Starch	Mater-Bi	Novamont, S.L.U. Novara-Italia	https: //www.novamontiberia.es/ (accessed on 20 November 2021) https://www.biobagusa.com (accessed on 20 November 2021)	
Starch-PBAT	BioAgri Mulch Film	BioBag Americas, Inc. Palm Harbor-Canadian		
Starch from the potato processing industry and/or grain, root or seed flour based resources	Solanyl®	Rodenburg Oosterhout- The Netherlands	https://biopolymers.nl (accessed on 20 November 2021)	

## 7. Conclusions and Future Perspectives

Commercial starch-based materials undoubtedly could play an important role in the food packaging industry as an environmentally friendly and sustainable alternative to synthetic packaging. However, their massive production for the food industry is still pending as these materials do not show the optical, barrier, and mechanical properties of their synthetic counterparts. Some research has been conducted to overcome these challenges, such as adapting and improving the usual thermoplastic processing techniques, physical and chemical modifications of starch, and blending with other biopolymers, plasticizers, and functional nano/micro fillers. The latter approach is also aimed at developing active or intelligent packaging to increase the food shelf life or act as a sensor during the food transport and storage chain.

On the other hand, the starch-based materials are biodegradable, however some chemical additives used to improve the end-product's performance could increase their longevity. Thus, new additives and polymers must be found to enhance the sustainability of forthcoming starch-based material, preferably from renewable resources. This allows their incorporation into the earth's ecological cycles when they reach the end of life stage in a managed, safe and sustainable way.

Author Contributions: Conceptualization, J.C., G.C.-B., S.R.L. and C.G.S.-H.; resources, J.C., A.Y.G.-L., G.C.-B., S.R.L., L.G.-G. and C.G.S.-H.; writing—original draft preparation, J.C., A.Y.G.-L., G.C.-B., S.R.L., L.G.-G. and C.G.S.-H.; writing—review and editing, J.C., G.C.-B., visualization, C.G.S.-H.; supervision, J.C.; project administration, J.C.; funding acquisition, G.C.-B. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research work was financially supported by ANID FONDECYT REGULAR project No. 1191528 (G.C.-B.), ANID CONICYT PIA/APOYO CCTE AFB170007 (G.C.-B.), FONDECYT REGULAR Project No. 1191651 (S.R.L. and J.C.). ANID International Collaboration Project REDES 190181. CIPA, ANID Regional, GORE BIO BIO, R17A10003, ACE210016, Fondef ID21110108.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

**Data Availability Statement:** The data that support the findings of this study are available from the corresponding author upon reasonable request.

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

## References

- 1. Plastics Europe; Conversio Market & Strategy GmbH. Plastics—The Facts 2019; Plastics Europe: Brussels, Belgium, 2019; pp. 14–35.
- 2. Waring, R.H.; Harris, R.; Mitchell, S. Plastic contamination of the food chain: A threat to human health? *Maturitas* **2018**, *115*, 64–68. [CrossRef]
- 3. Heredia-Guerrero, J.A.; Benítez, J.J.; Cataldi, P.; Paul, U.C.; Contardi, M.; Cingolani, R.; Bayer, I.S.; Heredia, A.; Athanassiou, A. All-natural sustainable packaging materials inspired by plant cuticles. *Adv. Sustain. Syst.* **2017**, *1*, 1600024. [CrossRef]
- Leite, L.S.; Bilatto, S.; Paschoalin, R.T.; Soares, A.C.; Moreira, F.K.; Oliveira, O.N., Jr.; Mattoso, L.H.; Bras, J. Eco-friendly gelatin films with rosin-grafted cellulose nanocrystals for antimicrobial packaging. *Int. J. Biol. Macromol.* 2020, 165, 2974–2983. [CrossRef] [PubMed]
- Patnaik, S.; Panda, A.K.; Kumar, S. Thermal degradation of corn starch based biodegradable plastic plates and determination of kinetic parameters by isoconversional methods using thermogravimetric analyzer. J. Energy Inst. 2020, 93, 1449–1459. [CrossRef]
- Marichelvam, M.; Jawaid, M.; Asim, M. Corn and rice starch-based bio-plastics as alternative packaging materials. *Fibers* 2019, 7, 32. [CrossRef]
- 7. Chen, J.; Wang, Y.; Liu, J.; Xu, X. Preparation, characterization, physicochemical property and potential application of porous starch: A review. *Int. J. Biol. Macromol.* **2020**, *148*, 1169–1181. [CrossRef]
- Di Filippo, M.F.; Dolci, L.S.; Liccardo, L.; Bigi, A.; Bonvicini, F.; Gentilomi, G.A.; Passerini, N.; Panzavolta, S.; Albertini, B. Cellulose derivatives-snail slime films: New disposable eco-friendly materials for food packaging. *Food Hydrocoll.* 2021, 111, 106247. [CrossRef]
- 9. Tapia-Blácido, D.; Sobral, P.J.; Menegalli, F.C. Development and characterization of biofilms based on Amaranth flour (*Amaranthus caudatus*). J. Food Eng. 2005, 67, 215–223. [CrossRef]
- 10. Parra, D.; Tadini, C.; Ponce, P.; Lugão, A. Mechanical properties and water vapor transmission in some blends of cassava starch edible films. *Carbohydr. Polym.* 2004, *58*, 475–481. [CrossRef]
- 11. Shamekh, S.; Myllärinen, P.; Poutanen, K.; Forssell, P. Film formation properties of potato starch hydrolysates. *Starch-Stärke* 2002, 54, 20–24. [CrossRef]
- 12. Yu, H.; Sabato, S.F.; D'Aprano, G.; Lacroix, M. Effect of the addition of CMC on the aggregation behaviour of proteins. *Radiat*. *Phys. Chem.* **2004**, *71*, 131–135. [CrossRef]
- Castaño, J.; Rodríguez-Llamazares, S.; Carrasco, C.; Bouza, R. Physical, chemical and mechanical properties of pehuen cellulosic husk and its pehuen-starch based composites. *Carbohydr. Polym.* 2012, 90, 1550–1556. [CrossRef] [PubMed]
- 14. Xu, Y.; Miladinov, V.; Hanna, M.A. Synthesis and characterization of starch acetates with high substitution. *Cereal Chem.* **2004**, *81*, 735–740. [CrossRef]
- 15. Thuwall, M.; Boldizar, A.; Rigdahl, M. Extrusion processing of high amylose potato starch materials. *Carbohydr. Polym.* **2006**, *65*, 441–446. [CrossRef]
- 16. Karki, S.; Kim, H.; Na, S.-J.; Shin, D.; Jo, K.; Lee, J. Thin films as an emerging platform for drug delivery. *Asian J. Pharm. Sci.* 2016, *11*, 559–574. [CrossRef]
- 17. Dufresne, A. Preparation and properties of cellulose nanomaterials. *Pap. Biomater.* **2020**, *5*, 1–13.
- 18. Le Corre, D.; Bras, J.; Dufresne, A. Starch nanoparticles: A review. Biomacromolecules 2010, 11, 1139–1153. [CrossRef]
- 19. Fan, X.; Zhang, S.; Lin, L.; Zhao, L.; Liu, A.; Wei, C. Properties of new starches from tubers of Arisaema elephas, yunnanense and erubescens. *Food Hydrocoll.* **2016**, *61*, 183–190. [CrossRef]
- Silva, A.P.M.; Oliveira, A.V.; Pontes, S.M.; Pereira, A.L.; Rosa, M.F.; Azeredo, H.M. Mango kernel starch films as affected by starch nanocrystals and cellulose nanocrystals. *Carbohydr. Polym.* 2019, 211, 209–216. [CrossRef]
- 21. Li, X.; Chen, W.; Chang, Q.; Zhang, Y.; Zheng, B.; Zeng, H. Structural and physicochemical properties of ginger (*Rhizoma curcumae* longae) starch and resistant starch: A comparative study. *Int. J. Biol. Macromol.* **2020**, *144*, 67–75. [CrossRef]
- 22. Hoover, R.; Hughes, T.; Chung, H.; Liu, Q. Composition, molecular structure, properties, and modification of pulse starches: A review. *Food Res. Int.* **2010**, *43*, 399–413. [CrossRef]
- Rodriguez-Garcia, M.E.; Hernandez-Landaverde, M.A.; Delgado, J.M.; Ramirez-Gutierrez, C.F.; Ramirez-Cardona, M.; Millan-Malo, B.M.; Londoño-Restrepo, S.M. Crystalline structures of the main components of starch. *Curr. Opin. Food Sci.* 2021, 37, 107–111. [CrossRef]
- 24. LeCorre, D.; Bras, J.; Dufresne, A. Influence of native starch's properties on starch nanocrystals thermal properties. *Carbohydr. Polym.* **2012**, *87*, 658–666. [CrossRef]
- 25. Almeida, M.R.; Alves, R.S.; Nascimbem, L.B.; Stephani, R.; Poppi, R.J.; de Oliveira, L.F.C. Determination of amylose content in starch using Raman spectroscopy and multivariate calibration analysis. *Anal. Bioanal. Chem.* **2010**, *397*, 2693–2701. [CrossRef]
- 26. Tester, R.F.; Karkalas, J.; Qi, X. Starch—Composition, fine structure and architecture. J. Cereal Sci. 2004, 39, 151–165. [CrossRef]
- Nordin, N.; Othman, S.H.; Rashid, S.A.; Basha, R.K. Effects of glycerol and thymol on physical, mechanical, and thermal properties of corn starch films. *Food Hydrocoll.* 2020, 106, 105884. [CrossRef]

- Freire, A.C.; Fertig, C.C.; Podczeck, F.; Veiga, F.; Sousa, J. Starch-based coatings for colon-specific drug delivery. Part I: The influence of heat treatment on the physico-chemical properties of high amylose maize starches. *Eur. J. Pharm. Biopharm.* 2009, 72, 574–586. [CrossRef] [PubMed]
- 29. Vamadevan, V.; Bertoft, E. Observations on the impact of amylopectin and amylose structure on the swelling of starch granules. *Food Hydrocoll.* **2020**, *103*, 105663. [CrossRef]
- Thiré, R.M.; Simão, R.A.; Andrade, C.T. High resolution imaging of the microstructure of maize starch films. *Carbohydr. Polym.* 2003, 54, 149–158. [CrossRef]
- Sindhu, R.; Devi, A.; Khatkar, B. Physicochemical, thermal and structural properties of heat moisture treated common buckwheat starches. J. Food Sci. Technol. 2019, 56, 2480–2489. [CrossRef] [PubMed]
- Condés, M.C.; Añón, M.C.; Dufresne, A.; Mauri, A.N. Composite and nanocomposite films based on amaranth biopolymers. *Food Hydrocoll.* 2018, 74, 159–167. [CrossRef]
- Condés, M.C.; Añón, M.C.; Mauri, A.N.; Dufresne, A. Amaranth protein films reinforced with maize starch nanocrystals. *Food Hydrocoll.* 2015, 47, 146–157. [CrossRef]
- da Silva, L.R.; de Carvalho, C.W.P.; Velasco, J.I.; Fakhouri, F.M. Extraction and characterization of starches from pigmented rice. Int. J. Biol. Macromol. 2020, 156, 485–493. [CrossRef] [PubMed]
- Li, C.; Dhital, S.; Gilbert, R.G.; Gidley, M.J. High-amylose wheat starch: Structural basis for water absorption and pasting properties. *Carbohydr. Polym* 2020, 245, 116557. [CrossRef]
- 36. Irani, M.; Abdel-Aal, E.-S.M.; Razavi, S.M.A.; Hucl, P.; Patterson, C.A. Thermal and Functional Properties of Hairless Canary Seed (*Phalaris canariensis* L.) Starch in Comparison with Wheat Starch. *Cereal Chem. J.* **2017**, *94*, 341–348. [CrossRef]
- Mukurumbira, A.; Mariano, M.; Dufresne, A.; Mellem, J.J.; Amonsou, E.O. Microstructure, thermal properties and crystallinity of amadumbe starch nanocrystals. *Int. J. Biol. Macromol.* 2017, 102, 241–247. [CrossRef]
- Cruz-Tirado, J.P.; Barros Ferreira, R.S.; Lizárraga, E.; Tapia-Blácido, D.R.; Silva, N.C.C.; Angelats-Silva, L.; Siche, R. Bioactive Andean sweet potato starch-based foam incorporated with oregano or thyme essential oil. *Food Packag. Shelf Life* 2020, 23, 100457. [CrossRef]
- Wang, H.; Yang, Q.; Ferdinand, U.; Gong, X.; Qu, Y.; Gao, W.; Ivanistau, A.; Feng, B.; Liu, M. Isolation and characterization of starch from light yellow, orange, and purple sweet potatoes. *Int. J. Biol. Macromol.* 2020, 160, 660–668. [CrossRef]
- Jiménez-Hernández, J.; Salazar-Montoya, J.A.; Ramos-Ramírez, E.G. Physical, chemical and microscopic characterization of a new starch from chayote (*Sechium edule*) tuber and its comparison with potato and maize starches. *Carbohydr. Polym.* 2007, 68, 679–686. [CrossRef]
- 41. Jamir, K.; Seshagirirao, K. Isolation, characterization and comparative study of starches from selected Zingiberaceae species, a non-conventional source. *Food Hydrocoll* **2017**, *72*, 247–253. [CrossRef]
- 42. Li, L.; Yuan, T.Z.; Setia, R.; Raja, R.B.; Zhang, B.; Ai, Y. Characteristics of pea, lentil and faba bean starches isolated from air-classified flours in comparison with commercial starches. *Food Chem.* **2019**, *276*, 599–607. [CrossRef]
- 43. Yniestra Marure, L.M.; Núñez-Santiago, M.C.; Agama-Acevedo, E.; Bello-Perez, L.A. Starch Characterization of Improved Chickpea Varieties Grown in Mexico. *Starch-Stärke* 2019, *71*, 1800139. [CrossRef]
- Saraiva Rodrigues, S.C.; Silva, A.S.d.; Carvalho, L.H.d.; Alves, T.S.; Barbosa, R. Morphological, structural, thermal properties of a native starch obtained from babassu mesocarp for food packaging application. *J. Mater. Res. Technol.* 2020, *9*, 15670–15678. [CrossRef]
- Harini, K.; Chandra Mohan, C.; Ramya, K.; Karthikeyan, S.; Sukumar, M. Effect of Punica granatum peel extracts on antimicrobial properties in Walnut shell cellulose reinforced Bio-thermoplastic starch films from cashew nut shells. *Carbohydr. Polym.* 2018, 184, 231–242. [CrossRef]
- 46. Zhang, Y.; Li, B.; Xu, F.; He, S.; Zhang, Y.; Sun, L.; Zhu, K.; Li, S.; Wu, G.; Tan, L. Jackfruit starch: Composition, structure, functional properties, modifications and applications. *Trends Food Sci. Technol.* **2021**, 107, 268–283. [CrossRef]
- Turola Barbi, R.C.; Teixeira, G.L.; Hornung, P.S.; Ávila, S.; Hoffmann-Ribani, R. Eriobotrya japonica seed as a new source of starch: Assessment of phenolic compounds, antioxidant activity, thermal, rheological and morphological properties. *Food Hydrocoll.* 2018, 77, 646–658. [CrossRef]
- 48. Macena, J.F.F.; Souza, J.C.A.d.; Camilloto, G.P.; Cruz, R.S. Physico-chemical, morphological and technological properties of the avocado (*Persea americana* Mill. cv. Hass) seed starch. *Ciênc. Agrotecnol.* **2020**, *44*, e001420. [CrossRef]
- 49. Shubeena; Wani, I.A.; Gani, A.; Sharma, P.; Wani, T.A.; Masoodi, F.A.; Hamdani, A.; Muzafar, S. Effect of acetylation on the physico-chemical properties of Indian Horse Chestnut (*Aesculus indica* L.) starch. *Starch-Stärke* 2015, 67, 311–318. [CrossRef]
- 50. Huneault, M.A.; Li, H. Preparation and properties of extruded thermoplastic starch/polymer blends. *J. Appl. Polym. Sci.* 2012, 126, E96–E108. [CrossRef]
- 51. Zobel, H.; Young, S.; Rocca, L. Starch gelatinization: An X-ray diffraction study. Cereal Chem. 1988, 65, 443–446.
- 52. Wang, T.L.; Bogracheva, T.Y.; Hedley, C.L. Starch: As simple as A, B, C? J. Exp. Bot. 1998, 49, 481–502. [CrossRef]
- 53. Pfannemüller, B. Influence of chain length of short monodisperse amyloses on the formation of A- and B-type X-ray diffraction patterns. *Int. J. Biol. Macromol.* **1987**, *9*, 105–108. [CrossRef]
- 54. Gidley, M.J.; Bulpin, P.V. Crystallisation of malto-oligosaccharides as models of the crystalline forms of starch: Minimum chain-length requirement for the formation of double helices. *Carbohydr. Res.* **1987**, *161*, 291–300. [CrossRef]

- 55. Srichuwong, S.; Isono, N.; Mishima, T.; Hisamatsu, M. Structure of lintnerized starch is related to X-ray diffraction pattern and susceptibility to acid and enzyme hydrolysis of starch granules. *Int. J. Biol. Macromol.* **2005**, 37, 115–121. [CrossRef] [PubMed]
- 56. Frost, K.; Kaminski, D.; Kirwan, G.; Lascaris, E.; Shanks, R. Crystallinity and structure of starch using wide angle X-ray scattering. *Carbohydr. Polym.* **2009**, *78*, 543–548. [CrossRef]
- 57. Kubo, A.; Yuguchi, Y.; Takemasa, M.; Suzuki, S.; Satoh, H.; Kitamura, S. The use of micro-beam X-ray diffraction for the characterization of starch crystal structure in rice mutant kernels of waxy, amylose extender, and sugary1. *J. Cereal Sci.* 2008, 48, 92–97. [CrossRef]
- 58. Mani, R.; Bhattacharya, M. Properties of injection moulded blends of starch and modified biodegradable polyesters. *Eur. Polym. J.* **2001**, *37*, 515–526. [CrossRef]
- Rosalina, I.; Bhattacharya, M. Dynamic rheological measurements and analysis of starch gels. *Carbohydr. Polym.* 2002, 48, 191–202. [CrossRef]
- Leelaphiwat, P.; Pechprankan, C.; Siripho, P.; Bumbudsanpharoke, N.; Harnkarnsujarit, N. Effects of nisin and EDTA on morphology and properties of thermoplastic starch and PBAT biodegradable films for meat packaging. *Food Chem.* 2022, 369, 130956. [CrossRef]
- 61. Noivoil, N.; Yoksan, R. Compatibility improvement of poly (lactic acid)/thermoplastic starch blown films using acetylated starch. *J. Appl. Polym. Sci.* **2021**, *138*, 49675. [CrossRef]
- 62. Yusoff, N.H.; Pal, K.; Narayanan, T.; de Souza, F.G. Recent trends on bioplastics synthesis and characterizations: Polylactic acid (PLA) incorporated with tapioca starch for packaging applications. *J. Mol. Struct.* **2021**, 1232, 129954. [CrossRef]
- 63. Zainal Abiddin, N.F.; Yusoff, A.; Ahmad, N. Effect of octenylsuccinylation on physicochemical, thermal, morphological and stability of octenyl succinic anhydride (OSA) modified sago starch. *Food Hydrocoll.* **2018**, 75, 138–146. [CrossRef]
- 64. Zheng, Y.; Hu, L.; Ding, N.; Liu, P.; Yao, C.; Zhang, H. Physicochemical and structural characteristics of the octenyl succinic ester of ginkgo starch. *Int. J. Biol. Macromol.* 2017, 94, 566–570. [CrossRef]
- 65. Bhandari, P.N.; Singhal, R.S. Effect of succinvlation on the corn and amaranth starch pastes. *Carbohydr. Polym.* **2002**, *48*, 233–240. [CrossRef]
- Dufresne, A.; Castaño, J. Polysaccharide nanomaterial reinforced starch nanocomposites: A review. *Starch-Stärke* 2017, 69, 1500307. [CrossRef]
- 67. Buléon, A.; Colonna, P.; Planchot, V.; Ball, S. Starch granules: Structure and biosynthesis. *Int. J. Biol. Macromol.* **1998**, *23*, 85–112. [CrossRef]
- 68. Xie, F.; Pollet, E.; Halley, P.J.; Avérous, L. Starch-based nano-biocomposites. Prog. Polym. Sci. 2013, 38, 1590–1628. [CrossRef]
- 69. Liu, D.; Wu, Q.; Chen, H.; Chang, P.R. Transitional properties of starch colloid with particle size reduction from micro-to nanometer. *J. Colloid Interface Sci.* 2009, 339, 117–124. [CrossRef] [PubMed]
- 70. Xiong, Z.; Ma, S.; Fan, L.; Tang, Z.; Zhang, R.; Na, H.; Zhu, J. Surface hydrophobic modification of starch with bio-based epoxy resins to fabricate high-performance polylactide composite materials. *Compos. Sci. Technol.* **2014**, *94*, 16–22. [CrossRef]
- 71. Ren, L.; Jiang, M.; Wang, L.; Zhou, J.; Tong, J. A method for improving dispersion of starch nanocrystals in water through crosslinking modification with sodium hexametaphosphate. *Carbohydr. Polym.* **2012**, *87*, 1874–1876. [CrossRef]
- 72. Aburto, J.; Hamaili, H.; Alric, E.; Borredon, E.; Gaset, A. *Advances in the Solvent-Free Synthesis of Fatty Esters of Starch*; INRA: Paris, France, 1999.
- 73. Kaur, B.; Ariffin, F.; Bhat, R.; Karim, A.A. Progress in starch modification in the last decade. *Food Hydrocoll.* **2012**, *26*, 398–404. [CrossRef]
- 74. Peñaranda Contreras, O.I.; Perilla Perilla, J.E.; Algecira Enciso, N.A. Revisión de la modificación química del almidón con ácidos orgánicos. *Ing. E Investig.* 2008, 28, 47–52.
- López, O.V.; Zaritzky, N.E.; García, M.A. Physicochemical characterization of chemically modified corn starches related to rheological behavior, retrogradation and film forming capacity. J. Food Eng. 2010, 100, 160–168. [CrossRef]
- 76. Rutenberg, M.W.; Solarek, D. Starch derivatives: Production and uses. In *Starch: Chemistry and Technology*; Elsevier: Amsterdam, The Netherlands, 1984; pp. 311–388.
- 77. Vanier, N.L.; El Halal, S.L.M.; Dias, A.R.G.; da Rosa Zavareze, E. Molecular structure, functionality and applications of oxidized starches: A review. *Food Chem.* 2017, 221, 1546–1559. [CrossRef] [PubMed]
- Sandhu, K.S.; Kaur, M.; Singh, N.; Lim, S.-T. A comparison of native and oxidized normal and waxy corn starches: Physicochemical, thermal, morphological and pasting properties. *LWT Food Sci. Technol.* 2008, 41, 1000–1010. [CrossRef]
- 79. Kushwaha, R.; Kaur, D. Recent techniques used in modification of starches: A review. In *Food Technology From Health to Wealth & Future Challenges*; Bharti Publication: Delhi, India, 2018; pp. 1–15.
- Lauer, M.K.; Smith, R.C. Recent advances in starch-based films toward food packaging applications: Physicochemical, mechanical, and functional properties. *Compr. Rev. Food Sci. Food Saf.* 2020, 19, 3031–3083. [CrossRef]
- Bangar, S.P.; Whiteside, W.S.; Ashogbon, A.O.; Kumar, M. Recent advances in thermoplastic starches for food packaging: A review. *Food Packag. Shelf Life* 2021, 30, 100743. [CrossRef]
- 82. Qin, Y.; Wang, W.; Zhang, H.; Dai, Y.; Hou, H.; Dong, H. Effects of citric acid on structures and properties of thermoplastic hydroxypropyl amylomaize starch films. *Materials* **2019**, *12*, 1565. [CrossRef]
- 83. Seligra, P.G.; Jaramillo, C.M.; Famá, L.; Goyanes, S. Biodegradable and non-retrogradable eco-films based on starch–Glycerol with citric acid as crosslinking agent. *Carbohydr. Polym.* **2016**, *138*, 66–74. [CrossRef]

- 84. Berski, W.; Ptaszek, A.; Ptaszek, P.; Ziobro, R.; Kowalski, G.; Grzesik, M.; Achremowicz, B. Pasting and rheological properties of oat starch and its derivatives. *Carbohydr. Polym.* 2011, *83*, 665–671. [CrossRef]
- 85. Zailani, M.A.; Kamilah, H.; Husaini, A.; Seruji, A.Z.R.A.; Sarbini, S.R. Functional and digestibility properties of sago (*Metroxylon sagu*) starch modified by microwave heat treatment. *Food Hydrocoll.* **2022**, *122*, 107042. [CrossRef]
- Zhong, Y.; Herburger, K.; Kirkensgaard, J.J.K.; Khakimov, B.; Hansen, A.R.; Blennow, A. Sequential maltogenic α-amylase and branching enzyme treatment to modify granular corn starch. *Food Hydrocoll.* 2021, 120, 106904. [CrossRef]
- 87. Rafiq, S.I.; Singh, S.; Saxena, D.C. Effect of heat-moisture and acid treatment on physicochemical, pasting, thermal and morphological properties of Horse Chestnut (*Aesculus indica*) starch. *Food Hydrocoll.* **2016**, *57*, 103–113. [CrossRef]
- 88. Kurdziel, M.; Królikowska, K.; Łabanowska, M.; Pietrzyk, S.; Michalec, M. The effect of thermal and irradiation treatments on structural and physicochemical properties of octenyl succinate maize starches. *Food Chem.* **2020**, *330*, 127242. [CrossRef] [PubMed]
- Cao, M.; Gao, Q. Internal structure of high degree substitution acetylated potato starch by chemical surface gelatinization. *Int. J. Biol. Macromol.* 2020, 145, 133–140. [CrossRef] [PubMed]
- 90. Ma, K.; Ngamwonglumlert, L.; Devahastin, S.; Chindapan, N.; Chiewchan, N. Feasibility study of the use of superheated steam spray drying to produce selected food powders. *Dry. Technol.* **2021**, *1*, 1–11. [CrossRef]
- Kurdziel, M.; Łabanowska, M.; Pietrzyk, S.; Sobolewska-Zielińska, J.; Michalec, M. Changes in the physicochemical properties of barley and oat starches upon the use of environmentally friendly oxidation methods. *Carbohydr. Polym.* 2019, 210, 339–349. [CrossRef] [PubMed]
- 92. Zou, J.; Xu, M.; Tang, W.; Wen, L.; Yang, B. Modification of structural, physicochemical and digestive properties of normal maize starch by thermal treatment. *Food Chem.* **2020**, *309*, 125733. [CrossRef]
- 93. Chung, Y.-L.; Ansari, S.; Estevez, L.; Hayrapetyan, S.; Giannelis, E.P.; Lai, H.-M. Preparation and properties of biodegradable starch–clay nanocomposites. *Carbohydr. Polym.* **2010**, *79*, 391–396. [CrossRef]
- 94. Xie, Y.; Zhang, B.; Li, M.-N.; Chen, H.-Q. Effects of cross-linking with sodium trimetaphosphate on structural and adsorptive properties of porous wheat starches. *Food Chem.* **2019**, *289*, 187–194. [CrossRef]
- Punia, S. Barley starch modifications: Physical, chemical and enzymatic—A review. Int. J. Biol. Macromol. 2020, 144, 578–585.
   [CrossRef]
- 96. Zhu, W.; Zheng, F.; Song, X.; Ren, H.; Gong, H. Influence of formulation parameters on lipid oxidative stability of Pickering emulsion stabilized by hydrophobically modified starch particles. *Carbohydr. Polym.* **2020**, *246*, 116649. [CrossRef]
- Bet, C.D.; de Oliveira, C.S.; Colman, T.A.D.; Marinho, M.T.; Lacerda, L.G.; Ramos, A.P.; Schnitzler, E. Organic amaranth starch: A study of its technological properties after heat-moisture treatment. *Food Chem.* 2018, 264, 435–442. [CrossRef] [PubMed]
- 98. Song, X.; Pei, Y.; Qiao, M.; Ma, F.; Ren, H.; Zhao, Q. Preparation and characterizations of Pickering emulsions stabilized by hydrophobic starch particles. *Food Hydrocoll.* **2015**, *45*, 256–263. [CrossRef]
- 99. Bharti, I.; Singh, S.; Saxena, D.C. Exploring the influence of heat moisture treatment on physicochemical, pasting, structural and morphological properties of mango kernel starches from Indian cultivars. *LWT* **2019**, *110*, 197–206. [CrossRef]
- 100. Li, S.; Zhang, B.; Tan, C.P.; Li, C.; Fu, X.; Huang, Q. Octenylsuccinate quinoa starch granule-stabilized Pickering emulsion gels: Preparation, microstructure and gelling mechanism. *Food Hydrocoll.* **2019**, *91*, 40–47. [CrossRef]
- 101. Hu, X.-P.; Zhang, B.; Jin, Z.-Y.; Xu, X.-M.; Chen, H.-Q. Effect of high hydrostatic pressure and retrogradation treatments on structural and physicochemical properties of waxy wheat starch. *Food Chem.* **2017**, 232, 560–565. [CrossRef] [PubMed]
- 102. Fonseca-Florido, H.; Vázquez-García, H.; Méndez-Montealvo, G.; Basilio-Cortés, U.; Navarro-Cortés, R.; Rodríguez-Marín, M.; Castro-Rosas, J.; Gómez-Aldapa, C. Effect of acid hydrolysis and OSA esterification of waxy cassava starch on emulsifying properties in Pickering-type emulsions. LWT 2018, 91, 258–264. [CrossRef]
- Sweedman, M.C.; Schäfer, C.; Gilbert, R.G. Aggregate and emulsion properties of enzymatically-modified octenylsuccinylated waxy starches. *Carbohydr. Polym.* 2014, 111, 918–927. [CrossRef]
- Ren, L.; Wang, Q.; Yan, X.; Tong, J.; Zhou, J.; Su, X. Dual modification of starch nanocrystals via crosslinking and esterification for enhancing their hydrophobicity. *Food Res. Int.* 2016, 87, 180–188. [CrossRef]
- 105. Putro, J.N.; Ismadji, S.; Gunarto, C.; Soetaredjo, F.E.; Ju, Y.H. A study of anionic, cationic, and nonionic surfactants modified starch nanoparticles for hydrophobic drug loading and release. *J. Mol. Liq.* **2020**, *298*, 112034. [CrossRef]
- 106. Sarmah, D.; Karak, N. Double network hydrophobic starch based amphoteric hydrogel as an effective adsorbent for both cationic and anionic dyes. *Carbohydr. Polym.* 2020, 242, 116320. [CrossRef]
- 107. Cova, A.; Sandoval, A.J.; Balsamo, V.; Müller, A.J. The effect of hydrophobic modifications on the adsorption isotherms of cassava starch. *Carbohydr. Polym.* 2010, *81*, 660–667. [CrossRef]
- 108. Barikani, M.; Mohammadi, M. Synthesis and characterization of starch-modified polyurethane. *Carbohydr. Polym.* 2007, 68, 773–780. [CrossRef]
- 109. Miskeen, S.; Hong, J.S.; Choi, H.-D.; Kim, J.-Y. Fabrication of citric acid-modified starch nanoparticles to improve their thermal stability and hydrophobicity. *Carbohydr. Polym.* **2021**, 253, 117242. [CrossRef]
- 110. Hu, X.; Jia, X.; Zhi, C.; Jin, Z.; Miao, M. Improving properties of normal maize starch films using dual-modification: Combination treatment of debranching and hydroxypropylation. *Int. J. Biol. Macromol.* **2019**, *130*, 197–202. [CrossRef]
- 111. Biduski, B.; da Silva, F.T.; da Silva, W.M.; El Halal, S.L.d.M.; Pinto, V.Z.; Dias, A.R.G.; da Rosa Zavareze, E. Impact of acid and oxidative modifications, single or dual, of sorghum starch on biodegradable films. *Food Chem.* **2017**, 214, 53–60. [CrossRef]

- 112. Biduski, B.; Evangelho, J.A.d.; Silva, F.T.d.; de Mello El Halal, S.L.; Takimi, A.S.; Carreño, N.L.V.; Dias, A.R.G.; Zavareze, E.d.R. Physicochemical properties of nanocomposite films made from sorghum-oxidized starch and nanoclay. *Starch-Stärke* 2017, 69, 1700079. [CrossRef]
- 113. Bergel, B.F.; Osorio, S.D.; da Luz, L.M.; Santana, R.M.C. Effects of hydrophobized starches on thermoplastic starch foams made from potato starch. *Carbohydr. Polym.* **2018**, 200, 106–114. [CrossRef]
- 114. La Fuente, C.I.; de Souza, A.T.; Tadini, C.C.; Augusto, P.E.D. Ozonation of cassava starch to produce biodegradable films. *Int. J. Biol. Macromol.* **2019**, 141, 713–720. [CrossRef] [PubMed]
- 115. Moin, A.; Ali, T.M.; Hasnain, A. Effect of succinvlation on functional and morphological properties of starches from broken kernels of Pakistani Basmati and Irri rice cultivars. *Food Chem.* **2016**, *191*, 52–58. [CrossRef] [PubMed]
- 116. Colussi, R.; Pinto, V.Z.; El Halal, S.L.M.; Biduski, B.; Prietto, L.; Castilhos, D.D.; da Rosa Zavareze, E.; Dias, A.R.G. Acetylated rice starches films with different levels of amylose: Mechanical, water vapor barrier, thermal, and biodegradability properties. *Food Chem.* 2017, 221, 1614–1620. [CrossRef]
- 117. Sifuentes-Nieves, I.; Neira-Velázquez, G.; Hernández-Hernández, E.; Barriga-Castro, E.; Gallardo-Vega, C.; Velazquez, G.; Mendez-Montealvo, G. Influence of gelatinization process and HMDSO plasma treatment on the chemical changes and water vapor permeability of corn starch films. *Int. J. Biol. Macromol.* 2019, 135, 196–202. [CrossRef]
- Sifuentes-Nieves, I.; Velazquez, G.; Flores-Silva, P.C.; Hernández-Hernández, E.; Neira-Velázquez, G.; Gallardo-Vega, C.; Mendez-Montealvo, G. HMDSO plasma treatment as alternative to modify structural properties of granular starch. *Int. J. Biol. Macromol.* 2020, 144, 682–689. [CrossRef]
- 119. Ding, Y.; Xiao, Y.; Ouyang, Q.; Luo, F.; Lin, Q. Modulating the in vitro digestibility of chemically modified starch ingredient by a non-thermal processing technology of ultrasonic treatment. *Ultrason. Sonochem.* **2021**, *70*, 105350. [CrossRef] [PubMed]
- 120. Nemţanu, M.R.; Braşoveanu, M. Exposure of starch to combined physical treatments based on corona electrical discharges and ionizing radiation. Impact on physicochemical properties. *Radiat. Phys. Chem.* **2021**, *184*, 109480. [CrossRef]
- 121. Li, Q.; Wu, Q.-Y.; Jiang, W.; Qian, J.-Y.; Zhang, L.; Wu, M.; Rao, S.-Q.; Wu, C.-S. Effect of pulsed electric field on structural properties and digestibility of starches with different crystalline type in solid state. *Carbohydr. Polym.* 2019, 207, 362–370. [CrossRef] [PubMed]
- 122. Kanatt, S.R. Irradiation as a tool for modifying tapioca starch and development of an active food packaging film with irradiated starch. *Radiat. Phys. Chem.* **2020**, *173*, 108873. [CrossRef]
- 123. Chung, K.M.; Moon, T.W.; Kim, H.; Chun, J.K. Physicochemical properties of sonicated mung bean, potato, and rice starches. *Cereal Chem.* **2002**, *79*, 631–633. [CrossRef]
- 124. Iida, Y.; Tuziuti, T.; Yasui, K.; Towata, A.; Kozuka, T. Control of viscosity in starch and polysaccharide solutions with ultrasound after gelatinization. *Innov. Food Sci. Emerg. Technol.* **2008**, *9*, 140–146. [CrossRef]
- 125. Goncalves, P.M.; Noreña, C.P.Z.; da Silveira, N.P.; Brandelli, A. Characterization of starch nanoparticles obtained from Araucaria angustifolia seeds by acid hydrolysis and ultrasound. *LWT-Food Sci. Technol.* **2014**, *58*, 21–27. [CrossRef]
- 126. Herceg, Z.; Batur, V.; Jambrak, A.R.; Badanjak, M.; Brnčić, S.R.; Lalas, V. Modification of rheological, thermophysical, textural and some physical properties of corn starch by tribomechanical treatment. *Carbohydr. Polym.* **2010**, *80*, 1072–1077. [CrossRef]
- 127. Zeng, F.; Gao, Q.-Y.; Han, Z.; Zeng, X.-A.; Yu, S.-J. Structural properties and digestibility of pulsed electric field treated waxy rice starch. *Food Chem.* **2016**, *194*, 1313–1319. [CrossRef] [PubMed]
- 128. Han, Z.; Zeng, X.-A.; Zhang, B.-S.; Yu, S.-J. Effects of pulsed electric fields (PEF) treatment on the properties of corn starch. *J. Food Eng.* **2009**, *93*, 318–323. [CrossRef]
- 129. Han, Z.; Yu, Q.; Zeng, X.A.; Luo, D.H.; Yu, S.J.; Zhang, B.S.; Chen, X.D. Studies on the microstructure and thermal properties of pulsed electric fields (PEF)-treated maize starch. *Int. J. Food Eng.* **2012**, *8*, 1–17. [CrossRef]
- 130. Maniglia, B.C.; Castanha, N.; Le-Bail, P.; Le-Bail, A.; Augusto, P.E.D. Starch modification through environmentally friendly alternatives: A review. *Crit. Rev. Food Sci. Nutr.* 2020, *61*, 2482–2505. [CrossRef] [PubMed]
- 131. Wardman, R.H.; Abdrabbo, A. Effect of plasma treatment on the spreading of micro drops through polylactic acid (PLA) and polyester (PET) fabrics. *Idea* 2010, *4*, 5.
- 132. Coles, R.; Kirwan, M.J. Food and Beverage Packaging Technology; John Wiley & Sons: Hoboken, NJ, USA, 2011.
- 133. Palai, B.; Biswal, M.; Mohanty, S.; Nayak, S.K. In situ reactive compatibilization of polylactic acid (PLA) and thermoplastic starch (TPS) blends; synthesis and evaluation of extrusion blown films thereof. *Ind. Crops Prod.* **2019**, *141*, 111748. [CrossRef]
- 134. Zhou, L.; Zhao, G.; Feng, Y.; Yin, J.; Jiang, W. Toughening polylactide with polyether-block-amide and thermoplastic starch acetate: Influence of starch esterification degree. *Carbohydr. Polym.* **2015**, *127*, 79–85. [CrossRef]
- Yang, Y.; Tang, Z.; Xiong, Z.; Zhu, J. Preparation and characterization of thermoplastic starches and their blends with poly (lactic acid). *Int. J. Biol. Macromol.* 2015, 77, 273–279. [CrossRef]
- Zeng, J.-B.; Li, K.-A.; Du, A.-K. Compatibilization strategies in poly(lactic acid)-based blends. RSC Adv. 2015, 5, 32546–32565.
   [CrossRef]
- 137. Nagarajan, V.; Mohanty, A.K.; Misra, M. Perspective on polylactic acid (PLA) based sustainable materials for durable applications: Focus on toughness and heat resistance. *ACS Sustain. Chem. Eng.* **2016**, *4*, 2899–2916. [CrossRef]
- 138. Gürler, N.; Paşa, S.; Temel, H. Silane doped biodegradable starch-PLA bilayer films for food packaging applications: Mechanical, thermal, barrier and biodegradability properties. *J. Taiwan Inst. Chem. Eng.* **2021**, *123*, 261–271. [CrossRef]

- 139. Li, Z.; Tan, B.H.; Lin, T.; He, C. Recent advances in stereocomplexation of enantiomeric PLA-based copolymers and applications. *Prog. Polym. Sci.* 2016, *62*, 22–72. [CrossRef]
- 140. Wootthikanokkhan, J.; Kasemwananimit, P.; Sombatsompop, N.; Kositchaiyong, A.; Isarankura na Ayutthaya, S.; Kaabbuathong, N. Preparation of modified starch-grafted poly (lactic acid) and a study on compatibilizing efficacy of the copolymers in poly (lactic acid)/thermoplastic starch blends. J. Appl. Polym. Sci. 2012, 126, E389–E396. [CrossRef]
- 141. Witt, U.; Yamamoto, M.; Seeliger, U.; Müller, R.J.; Warzelhan, V. Biodegradable polymeric materials—Not the origin but the chemical structure determines biodegradability. *Angew. Chem. Int. Ed.* **1999**, *38*, 1438–1442. [CrossRef]
- 142. Wei, D.; Wang, H.; Xiao, H.; Zheng, A.; Yang, Y. Morphology and mechanical properties of poly (butylene adipate-coterephthalate)/potato starch blends in the presence of synthesized reactive compatibilizer or modified poly (butylene adipate-coterephthalate). *Carbohydr. Polym.* **2015**, *123*, 275–282. [CrossRef]
- 143. Wangprasertkul, J.; Siriwattanapong, R.; Harnkarnsujarit, N. Antifungal packaging of sorbate and benzoate incorporated biodegradable films for fresh noodles. *Food Control* **2021**, *123*, 107763. [CrossRef]
- Fourati, Y.; Tarrés, Q.; Mutjé, P.; Boufi, S. PBAT/thermoplastic starch blends: Effect of compatibilizers on the rheological, mechanical and morphological properties. *Carbohydr. Polym.* 2018, 199, 51–57. [CrossRef] [PubMed]
- 145. Tănase, E.E.; Popa, M.E.; Râpă, M.; Popa, O. Preparation and characterization of biopolymer blends based on polyvinyl alcohol and starch. *Rom. Biotechnol. Lett.* **2015**, *20*, 10307.
- 146. Srinivasa, P.; Ramesh, M.; Kumar, K.; Tharanathan, R. Properties and sorption studies of chitosan–Polyvinyl alcohol blend films. *Carbohydr. Polym.* **2003**, *53*, 431–438. [CrossRef]
- 147. Follain, N.; Joly, C.; Dole, P.; Bliard, C. Properties of starch based blends. Part 2. Influence of poly vinyl alcohol addition and photocrosslinking on starch based materials mechanical properties. *Carbohydr. Polym.* **2005**, *60*, 185–192. [CrossRef]
- 148. Ismail, H.; Zaaba, N.F. The mechanical properties, water resistance and degradation behaviour of silica-filled sago starch/PVA plastic films. *J. Elastomers Plast.* **2014**, *46*, 96–109. [CrossRef]
- 149. Syamani, F.A.; Kusumaningrum, W.B.; Akbar, F.; Ismadi; Widyaningrum, B.A.; Pramasari, D.A. Characteristics of bioplastic made from modified cassava starch with addition of polyvinyl alcohol. *IOP Conf. Ser. Earth Environ. Sci.* 2020, 591, 012016. [CrossRef]
- 150. Arboleda, G.A.; Montilla, C.E.; Villada, H.S.; Varona, G.A. Obtaining a Flexible Film Elaborated from Cassava Thermoplastic Starch and Polylactic Acid. *Int. J. Polym. Sci.* 2015, 2015, 627268. [CrossRef]
- 151. Chen, G.; Wei, M.; Chen, J.; Huang, J.; Dufresne, A.; Chang, P.R. Simultaneous reinforcing and toughening: New nanocomposites of waterborne polyurethane filled with low loading level of starch nanocrystals. *Polymer* **2008**, *49*, 1860–1870. [CrossRef]
- 152. Nayak, S.K. Biodegradable PBAT/Starch Nanocomposites. *Polym. -Plast. Technol. Eng.* 2010, 49, 1406–1418. [CrossRef]
- 153. Zhou, J.; Ma, Y.; Ren, L.; Tong, J.; Liu, Z.; Xie, L. Preparation and characterization of surface crosslinked TPS/PVA blend films. *Carbohydr. Polym.* **2009**, *76*, 632–638. [CrossRef]
- 154. Kahvand, F.; Fasihi, M. Plasticizing and anti-plasticizing effects of polyvinyl alcohol in blend with thermoplastic starch. *Int. J. Biol. Macromol.* **2019**, 140, 775–781. [CrossRef]
- 155. Liu, Z.; Jiang, M.; Bai, X.; Dong, X.; Tong, J.; Zhou, J. Effect of postcrosslinking modification with glutaraldehyde on the properties of thermoplastic starch/poly(vinyl alcohol) blend films. *J. Appl. Polym. Sci.* **2012**, *124*, 3774–3781. [CrossRef]
- 156. Negim, E.S.M.; Rakhmetullayeva, R.K.; Yeligbayeva, G.Z.; Urkimbaeva, P.I.; Primzharova, S.T.; Kaldybekov, D.B.; Khatib, J.M.; Mun, G.A.; Craig, W. Improving biodegradability of polyvinyl alcohol/starch blend films for packaging applications. *Int. J. Basic Appl. Sci.* 2014, *3*, 263. [CrossRef]
- 157. Wang, D.-W.; Sun, L.-S.; Peng, X.-L.; Runt, J.; Kuo, M.-C.; Huang, K.-S.; Yeh, J.-T. Tapioca/polyvinyl alcohol thermoplastic starch materials processed with the aid of supercritical CO2. *Food Packag. Shelf Life* **2019**, *22*, 100425. [CrossRef]
- 158. Xu, Y.; Kim, K.M.; Hanna, M.A.; Nag, D. Chitosan–Starch composite film: Preparation and characterization. *Ind. Crops Prod.* 2005, 21, 185–192. [CrossRef]
- 159. Vásconez, M.B.; Flores, S.K.; Campos, C.A.; Alvarado, J.; Gerschenson, L.N. Antimicrobial activity and physical properties of chitosan-tapioca starch based edible films and coatings. *Food Res. Int.* **2009**, *42*, 762–769. [CrossRef]
- 160. Tuhin, M.O.; Rahman, N.; Haque, M.E.; Khan, R.A.; Dafader, N.C.; Islam, R.; Nurnabi, M.; Tonny, W. Modification of mechanical and thermal property of chitosan–starch blend films. *Radiat. Phys. Chem.* **2012**, *81*, 1659–1668. [CrossRef]
- Li, H.; Gao, X.; Wang, Y.; Zhang, X.; Tong, Z. Comparison of chitosan/starch composite film properties before and after cross-linking. *Int. J. Biol. Macromol.* 2013, 52, 275–279. [CrossRef]
- 162. Liu, H.; Adhikari, R.; Guo, Q.; Adhikari, B. Preparation and characterization of glycerol plasticized (high-amylose) starch–chitosan films. *J. Food Eng.* **2013**, *116*, 588–597. [CrossRef]
- Pavoni, J.M.F.; Luchese, C.L.; Tessaro, I.C. Impact of acid type for chitosan dissolution on the characteristics and biodegradability of cornstarch/chitosan based films. *Int. J. Biol. Macromol.* 2019, 138, 693–703. [CrossRef]
- 164. Hubackova, J.; Dvorackova, M.; Svoboda, P.; Mokrejs, P.; Kupec, J.; Pozarova, I.; Alexy, P.; Bugaj, P.; Machovsky, M.; Koutny, M. Influence of various starch types on PCL/starch blends anaerobic biodegradation. *Polym. Test.* 2013, 32, 1011–1019. [CrossRef]
- 165. Ikeo, Y.; Aoki, K.; Kishi, H.; Matsuda, S.; Murakami, A. Nano clay reinforced biodegradable plastics of PCL starch blends. *Polym. Adv. Technol.* **2006**, *17*, 940–944. [CrossRef]
- 166. Rosa, D.S.; Guedes, C.G.F.; Pedroso, A.G.; Calil, M.R. The influence of starch gelatinization on the rheological, thermal, and morphological properties of poly(ε-caprolactone) with corn starch blends. *Mater. Sci. Eng.* C 2004, 24, 663–670. [CrossRef]

- 167. Cho, H.; Moon, H.; Kim, M.; Nam, K.; Kim, J. Biodegradability and biodegradation rate of poly (caprolactone)-starch blend and poly (butylene succinate) biodegradable polymer under aerobic and anaerobic environment. *Waste Manag.* 2011, 31, 475–480. [CrossRef]
- Rosa, D.S.; Guedes, C.G.; Casarin, F. Mechanical Behavior and Biodegradation of Poly (ε-caprolactone)/Starch Blends with and without Expansor. *Polym. Bull.* 2005, 54, 321–333. [CrossRef]
- 169. Wu, C.-S. Physical properties and biodegradability of maleated-polycaprolactone/starch composite. *Polym. Degrad. Stab.* **2003**, *80*, 127–134. [CrossRef]
- Carvalho, A.F.; Job, A.; Alves, N.; Curvelo, A.A.S.; Gandini, A. Thermoplastic starch/natural rubber blends. *Carbohydr. Polym.* 2003, 53, 95–99. [CrossRef]
- 171. Trovatti, E.; Carvalho, A.J.F.; Gandini, A. A new approach to blending starch with natural rubber. *Polym. Int.* **2015**, *64*, 605–610. [CrossRef]
- 172. Cai, Z.; Čadek, D.; Šmejkalová, P.; Kadeřábková, A.; Nová, M.; Kuta, A. The modification of properties of thermoplastic starch materials: Combining potato starch with natural rubber and epoxidized natural rubber. *Mater. Today Commun.* 2021, 26, 101912. [CrossRef]
- 173. Jantanasakulwong, K.; Leksawasdi, N.; Seesuriyachan, P.; Wongsuriyasak, S.; Techapun, C.; Ougizawa, T. Reactive blending of thermoplastic starch, epoxidized natural rubber and chitosan. *Eur. Polym. J.* **2016**, *84*, 292–299. [CrossRef]
- 174. Saetun, V.; Chiachun, C.; Riyajan, S.-A.; Kaewtatip, K. Green composites based on thermoplastic starch and rubber wood sawdust. *Polym. Compos.* **2017**, *38*, 1063–1069. [CrossRef]
- 175. Cheong, K.S.; Balasubramaniam, J.-R.; Hung, Y.P.; Chuong, W.S.; Amartalingam, R. Development of biodegradable plastic composite blends based on sago derived starch and natural rubber. *Pertanika J. Sci. Technol.* **2010**, *18*, 411–420.
- 176. Riyajan, S.-A.; Patisat, S. A novel packaging film from cassava starch and natural rubber. *J. Polym. Environ.* **2018**, *26*, 2845–2854. [CrossRef]
- 177. Wang, S.; Yu, J.; Yu, J. Preparation and characterization of compatible thermoplastic starch/polyethylene blends. *Polym. Degrad. Stab.* **2005**, *87*, 395–401. [CrossRef]
- 178. Mazerolles, T.; Heuzey, M.-C.; Soliman, M.; Martens, H.; Kleppinger, R.; Huneault, M.A. Development of multilayer barrier films of thermoplastic starch and low-density polyethylene. *J. Polym. Res.* **2020**, *27*, 44. [CrossRef]
- 179. Arvanitoyannisa, I.; Biliaderis, C.; Ogawab, H.; Kawasakib, N. Biodegradable films made from low-density polyethylene (LDPE), rice starch and potato starch for food packaging applications: Part 1. *Carbohydr. Polym.* **1998**, *36*, 89–104. [CrossRef]
- 180. Lisdayana, N.; Fahma, F.; Sunarti, T.C.; Iriani, E.S. Thermoplastic starch–PVA nanocomposite films reinforced with nanocellulose from oil palm empty fruit bunches (OPEFBs): Effect of starch type. *J. Nat. Fibers* **2020**, *17*, 1069–1080. [CrossRef]
- Heidarian, P.; Behzad, T.; Sadeghi, M. Investigation of cross-linked PVA/starch biocomposites reinforced by cellulose nanofibrils isolated from aspen wood sawdust. *Cellulose* 2017, 24, 3323–3339. [CrossRef]
- Keshk, S.M.; El-Zahhar, A.A.; Haija, M.A.; Bondock, S. Synthesis of a magnetic nanoparticles/dialdehyde starch-based composite film for food packaging. *Starch-Stärke* 2019, *71*, 1800035. [CrossRef]
- 183. Fahma, F.; Sunarti, T.C.; Indriyani, S.M.; Lisdayana, N. Thermoplastic cassava starch-PVA composite films with cellulose nanofibers from oil palm empty fruit bunches as reinforcement agent. *Int. J. Polym. Sci.* 2017, 2017, 2745721. [CrossRef]
- 184. Fahma, F.; Lisdayana, N.; Abidin, Z.; Noviana, D.; Sari, Y.W.; Mukti, R.R.; Yunus, M.; Kusumaatmaja, A.; Kadja, G.T.M. Nanocellulose-based fibres derived from palm oil by-products and their in vitro biocompatibility analysis. *J. Text. Inst.* 2020, 111, 1354–1363. [CrossRef]
- Khondkar, D.; Tester, R.F.; Hudson, N.; Karkalas, J.; Morrow, J. Rheological behaviour of uncross-linked and cross-linked gelatinised waxy maize starch with pectin gels. *Food Hydrocoll.* 2007, 21, 1296–1301. [CrossRef]
- Guadarrama-Lezama, A.Y.; Castaño, J.; Velázquez, G.; Carrillo-Navas, H.; Alvarez-Ramírez, J. Effect of nopal mucilage addition on physical, barrier and mechanical properties of citric pectin-based films. J. Food Sci. Technol. 2018, 55, 3739–3748. [CrossRef]
- 187. Voragen, A.G.J.; Coenen, G.-J.; Verhoef, R.P.; Schols, H.A. Pectin, a versatile polysaccharide present in plant cell walls. *Struct. Chem.* 2009, *20*, 263–275. [CrossRef]
- 188. Coffin, D.R.; Fishman, M.L. Physical and mechanical properties of highly plasticized pectin/starch films. *J. Appl. Polym. Sci.* **1994**, 54, 1311–1320. [CrossRef]
- 189. Sabando, C.; Ide, W.; Rodríguez-Díaz, M.; Cabrera-Barjas, G.; Castaño, J.; Bouza, R.; Müller, N.; Gutiérrez, C.; Barral, L.; Rojas, J. A novel hydrocolloid film based on pectin, starch and *Gunnera tinctoria* and *Ugni molinae* plant extracts for wound dressing applications. *Curr. Top. Med. Chem.* 2020, 20, 280–292. [CrossRef]
- Carreño, G.; Marican, A.; Vijayakumar, S.; Valdés, O.; Cabrera-Barjas, G.; Castaño, J.; Durán-Lara, E.F. Sustained release of linezolid from prepared hydrogels with polyvinyl alcohol and aliphatic dicarboxylic acids of variable chain lengths. *Pharmaceutics* 2020, 12, 982. [CrossRef] [PubMed]
- 191. Pang, M.M.; Pun, M.Y.; Ishak, Z.A.M. Degradation studies during water absorption, aerobic biodegradation, and soil burial of biobased thermoplastic starch from agricultural waste/polypropylene blends. J. Appl. Polym. Sci. 2013, 129, 3656–3664. [CrossRef]
- 192. Chandra, R.; Rustgi, R. Biodegradation of maleated linear low-density polyethylene and starch blends. *Polym. Degrad. Stab.* **1997**, 56, 185–202. [CrossRef]
- 193. Raee, E.; Avid, A.; Kaffashi, B. Effect of compatibilizer concentration on dynamic rheological behavior and morphology of thermoplastic starch/polypropylene blends. *J. Appl. Polym. Sci.* 2020, 137, 48742. [CrossRef]

- Martins, A.B.; Santana, R.M.C. Effect of carboxylic acids as compatibilizer agent on mechanical properties of thermoplastic starch and polypropylene blends. *Carbohydr. Polym.* 2016, 135, 79–85. [CrossRef]
- 195. Tabasum, S.; Younas, M.; Zaeem, M.A.; Majeed, I.; Majeed, M.; Noreen, A.; Iqbal, M.N.; Zia, K.M. A review on blending of corn starch with natural and synthetic polymers, and inorganic nanoparticles with mathematical modeling. *Int. J. Biol. Macromol.* 2019, 122, 969–996. [CrossRef] [PubMed]
- 196. Ostafińska, A.; Mikešová, J.; Krejčíková, S.; Nevoralová, M.; Šturcová, A.; Zhigunov, A.; Michálková, D.; Šlouf, M. Thermoplastic starch composites with TiO<sub>2</sub> particles: Preparation, morphology, rheology and mechanical properties. *Int. J. Biol. Macromol.* 2017, 101, 273–282. [CrossRef] [PubMed]
- 197. Pan, H.; Xu, D.; Liu, Q.; Ren, H.Q.; Zhou, M. Preparation and characterization of corn starch-nanodiamond composite films. *Appl. Mech. Mater.* **2014**, 469, 156–161. [CrossRef]
- 198. Hammache, Y.; Serier, A.; Chaoui, S. The effect of thermoplastic starch on the properties of polypropylene/high density polyethylene blend reinforced by nano-clay. *Mater. Res. Express* **2020**, *7*, 025308. [CrossRef]
- Toumi, N.; Guessoum, M.; Nekkaa, S. Biocomposites based on date palm flour reinforced (70/30) polypropylene/thermoplastic starch blend: Effects of flour treatment and selective dispersion. J. Adhes. Sci. Technol. 2019, 33, 2071–2092. [CrossRef]
- Campos-Requena, V.H.; Rivas, B.L.; Pérez, M.A.; Figueroa, C.R.; Figueroa, N.E.; Sanfuentes, E.A. Thermoplastic starch/clay nanocomposites loaded with essential oil constituents as packaging for strawberries – In vivo antimicrobial synergy over Botrytis cinerea. *Postharvest Biol. Technol.* 2017, 129, 29–36. [CrossRef]
- Javanbakht, S.; Namazi, H. Solid state photoluminescence thermoplastic starch film containing graphene quantum dots. *Carbohydr. Polym.* 2017, 176, 220–226. [CrossRef]
- Liu, Y.; Fan, L.; Mo, X.; Yang, F.; Pang, J. Effects of nanosilica on retrogradation properties and structures of thermoplastic cassava starch. J. Appl. Polym. Sci. 2018, 135, 45687. [CrossRef]
- Liu, Q.; Li, F.; Lu, H.; Li, M.; Liu, J.; Zhang, S.; Sun, Q.; Xiong, L. Enhanced dispersion stability and heavy metal ion adsorption capability of oxidized starch nanoparticles. *Food Chem.* 2018, 242, 256–263. [CrossRef]
- Sarkar, A.; Biswas, D.R.; Datta, S.C.; Dwivedi, B.S.; Bhattacharyya, R.; Kumar, R.; Bandyopadhyay, K.K.; Saha, M.; Chawla, G.; Saha, J.K. Preparation of novel biodegradable starch/poly (vinyl alcohol)/bentonite grafted polymeric films for fertilizer encapsulation. *Carbohydr. Polym.* 2021, 259, 117679. [CrossRef] [PubMed]
- 205. Lendvai, L.; Apostolov, A.; Karger-Kocsis, J. Characterization of layered silicate-reinforced blends of thermoplastic starch (TPS) and poly (butylene adipate-co-terephthalate). *Carbohydr. Polym.* **2017**, *173*, 566–572. [CrossRef]
- Islam, H.B.M.Z.; Susan, M.A.B.H.; Imran, A.B. High-strength potato starch/hectorite clay-based nanocomposite film: Synthesis and characterization. *Iran. Polym. J.* 2021, 30, 513–521. [CrossRef]
- 207. Khodaeimehr, R.; Peighambardoust, S.J.; Peighambardoust, S.H. Preparation and characterization of corn starch/clay nanocomposite films: Effect of clay content and surface modification. *Starch-Stärke* 2018, 70, 1700251. [CrossRef]
- Teoh, K.H.; Ramesh, S.; Arof, A.K. Investigation on the effect of nanosilica towards corn starch–lithium perchlorate-based polymer electrolytes. J. Solid State Electrochem. 2012, 16, 3165–3170. [CrossRef]
- López, O.V.; Castillo, L.A.; Garcia, M.A.; Villar, M.A.; Barbosa, S.E. Food packaging bags based on thermoplastic corn starch reinforced with talc nanoparticles. *Food Hydrocoll.* 2015, 43, 18–24. [CrossRef]
- 210. Menzel, C. Improvement of starch films for food packaging through a three-principle approach: Antioxidants, cross-linking and reinforcement. *Carbohydr. Polym.* 2020, 250, 116828. [CrossRef]
- Wu, J.; Du, X.; Yin, Z.; Xu, S.; Xu, S.; Zhang, Y. Preparation and characterization of cellulose nanofibrils from coconut coir fibers and their reinforcements in biodegradable composite films. *Carbohydr. Polym.* 2019, 211, 49–56. [CrossRef]
- 212. Michel, A.; Billington, S. Characterization of poly-hydroxybutyrate films and hemp fiber reinforced composites exposed to accelerated weathering. *Polym. Degrad. Stab.* **2012**, *97*, 870–878. [CrossRef]
- Ochoa-Yepes, O.; Medina-Jaramillo, C.; Guz, L.; Famá, L. Biodegradable and edible starch composites with fiber-rich lentil flour to use as food packaging. *Starch-Stärke* 2018, 70, 1700222. [CrossRef]
- Glenn, G.M.; Klamczynski, A.; Holtman, K.M.; Chiou, B.-S.; Orts, W.J.; Wood, D. Cellulose fiber reinforced starch-based foam composites. J. Biobased Mater. Bioenergy 2007, 1, 360–366. [CrossRef]
- 215. Avérous, L.; Fringant, C.; Moro, L. Plasticized starch–cellulose interactions in polysaccharide composites. *Polymer* 2001, 42, 6565–6572. [CrossRef]
- Versino, F.; García, M.A. Cassava (*Manihot esculenta*) starch films reinforced with natural fibrous filler. *Ind. Crops Prod.* 2014, 58, 305–314. [CrossRef]
- Liu, W.; Drzal, L.T.; Mohanty, A.K.; Misra, M. Influence of processing methods and fiber length on physical properties of kenaf fiber reinforced soy based biocomposites. *Compos. Part B Eng.* 2007, 38, 352–359. [CrossRef]
- Susmitha, A.; Sasikumar, K.; Rajan, D.; Padmakumar, M.A.; Nampoothiri, K.M. Development and characterization of corn starch-gelatin based edible films incorporated with mango and pineapple for active packaging. *Food Biosci.* 2021, 41, 100977. [CrossRef]
- 219. Meng, L.; Xie, F.; Zhang, B.; Wang, D.K.; Yu, L. Natural biopolymer alloys with superior mechanical properties. *ACS Sustain. Chem. Eng.* **2018**, *7*, 2792–2802. [CrossRef]
- 220. Yao, X.; Qin, Y.; Zhang, M.; Zhang, J.; Qian, C.; Liu, J. Development of active and smart packaging films based on starch, polyvinyl alcohol and betacyanins from different plant sources. *Int. J. Biol. Macromol.* **2021**, *183*, 358–368. [CrossRef]

- Vianna, T.C.; Marinho, C.O.; Marangoni Junior, L.; Ibrahim, S.A.; Vieira, R.P. Essential oils as additives in active starch-based food packaging films: A review. *Int. J. Biol. Macromol.* 2021, 182, 1803–1819. [CrossRef]
- Acosta, S.; Chiralt, A.; Santamarina, P.; Rosello, J.; González-Martínez, C.; Cháfer, M. Antifungal films based on starch-gelatin blend, containing essential oils. *Food Hydrocoll.* 2016, 61, 233–240. [CrossRef]
- 223. Souza, A.G.; Ferreira, R.R.; Paula, L.C.; Mitra, S.K.; Rosa, D.S. Starch-based films enriched with nanocellulose-stabilized Pickering emulsions containing different essential oils for possible applications in food packaging. *Food Packag. Shelf Life* 2021, 27, 100615. [CrossRef]
- 224. Raigond, P.; Sood, A.; Kalia, A.; Joshi, A.; Kaundal, B.; Raigond, B.; Dutt, S.; Singh, B.; Chakrabarti, S.K. Antimicrobial Activity of Potato Starch-Based Active Biodegradable Nanocomposite Films. *Potato Res.* **2019**, *62*, 69–83. [CrossRef]
- 225. Kumar, P.; Tanwar, R.; Gupta, V.; Upadhyay, A.; Kumar, A.; Gaikwad, K.K. Pineapple peel extract incorporated poly(vinyl alcohol)-corn starch film for active food packaging: Preparation, characterization and antioxidant activity. *Int. J. Biol. Macromol.* 2021, 187, 223–231. [CrossRef] [PubMed]
- Song, X.; Zuo, G.; Chen, F. Effect of essential oil and surfactant on the physical and antimicrobial properties of corn and wheat starch films. *Int. J. Biol. Macromol.* 2018, 107, 1302–1309. [CrossRef] [PubMed]
- 227. Lozano-Navarro, J.I.; Díaz-Zavala, N.P.; Velasco-Santos, C.; Melo-Banda, J.A.; Páramo-García, U.; Paraguay-Delgado, F.; García-Alamilla, R.; Martínez-Hernández, A.L.; Zapién-Castillo, S. Chitosan-Starch Films with Natural Extracts: Physical, Chemical, Morphological and Thermal Properties. *Materials* 2018, 11, 120. [CrossRef] [PubMed]
- Torres Vargas, O.L.; Galeano Loaiza, Y.V.; González, M.L. Effect of incorporating extracts from natural pigments in alginate/starch films. J. Mater. Res. Technol. 2021, 13, 2239–2250. [CrossRef]
- 229. Mei, J.; Yuan, Y.; Wu, Y.; Li, Y. Characterization of edible starch–chitosan film and its application in the storage of Mongolian cheese. *Int. J. Biol. Macromol.* **2013**, *57*, 17–21. [CrossRef] [PubMed]
- Iamareerat, B.; Singh, M.; Sadiq, M.B.; Anal, A.K. Reinforced cassava starch based edible film incorporated with essential oil and sodium bentonite nanoclay as food packaging material. *J. Food Sci. Technol.* 2018, 55, 1953–1959. [CrossRef]
- Jamróz, E.; Juszczak, L.; Kucharek, M. Investigation of the physical properties, antioxidant and antimicrobial activity of ternary potato starch-furcellaran-gelatin films incorporated with lavender essential oil. *Int. J. Biol. Macromol.* 2018, 114, 1094–1101. [CrossRef]
- 232. Utami, R.; Khasanah, L.U.; Manuhara, G.J.; Ayuningrum, Z.K. Effects of Cinnamon Bark Essential Oil (*Cinnamomum burmannii*) on Characteristics of Edible Film and Quality of Fresh Beef. *Pertanika J. Trop. Agric. Sci.* **2019**, *42*, 1173–1184.
- Aitboulahsen, M.; El Galiou, O.; Laglaoui, A.; Bakkali, M.; Hassani Zerrouk, M. Effect of plasticizer type and essential oils on mechanical, physicochemical, and antimicrobial characteristics of gelatin, starch, and pectin-based films. *J. Food Processing Preserv.* 2020, 44, e14480. [CrossRef]
- 234. De Souza, A.G.; Dos Santos, N.M.A.; da Silva Torin, R.F.; Dos Santos Rosa, D. Synergic antimicrobial properties of Carvacrol essential oil and montmorillonite in biodegradable starch films. *Int. J. Biol. Macromol.* **2020**, *164*, 1737–1747. [CrossRef]
- 235. De Oliveira Filho, J.G.; Albiero, B.R.; Cipriano, L.; de Oliveira Nobre Bezerra, C.C.; Oldoni, F.C.A.; Egea, M.B.; de Azeredo, H.M.C.; Ferreira, M.D. Arrowroot starch-based films incorporated with a carnauba wax nanoemulsion, cellulose nanocrystals, and essential oils: A new functional material for food packaging applications. *Cellulose* 2021, 28, 6499–6511. [CrossRef]
- Cai, C.; Ma, R.; Duan, M.; Deng, Y.; Liu, T.; Lu, D. Effect of starch film containing thyme essential oil microcapsules on physicochemical activity of mango. *LWT* 2020, *131*, 109700. [CrossRef]
- 237. Cano, A.; Cháfer, M.; Chiralt, A.; González-Martínez, C. Physical and Antimicrobial Properties of Starch-PVA Blend Films as Affected by the Incorporation of Natural Antimicrobial Agents. *Foods* **2016**, *5*, 3. [CrossRef]
- 238. Meng, Q.; Liu, Z.; Han, S.; Xu, L.; Araby, S.; Cai, R.; Zhao, Y.; Lu, S.; Liu, T. A facile approach to fabricate highly sensitive, flexible strain sensor based on elastomeric/graphene platelet composite film. *J. Mater. Sci.* **2019**, *54*, 10856–10870. [CrossRef]
- 239. Kumari, A.; Yadav, S.K.; Yadav, S.C. Biodegradable polymeric nanoparticles based drug delivery systems. *Colloids Surf. B Biointerfaces* **2010**, *75*, 1–18. [CrossRef]
- 240. Yu, M.; Ji, N.; Wang, Y.; Dai, L.; Xiong, L.; Sun, Q. Starch-based nanoparticles: Stimuli responsiveness, toxicity, and interactions with food components. *Compr. Rev. Food Sci. Food Saf.* **2021**, 20, 1075–1100. [CrossRef]
- 241. Dufresne, A.; Kellerhals, M.B.; Witholt, B. Transcrystallization in Mcl-PHAs/cellulose whiskers composites. *Macromolecules* **1999**, 32, 7396–7401. [CrossRef]
- Lin, H.; Qin, L.Z.; Hong, H.; Li, Q. Preparation of starch nanoparticles via high-energy ball milling. J. Nano Res. 2016, 40, 174–179. [CrossRef]
- Chen, C.-J.; Shen, Y.-C.; Yeh, A.-I. Physico-chemical characteristics of media-milled corn starch. J. Agric. Food Chem. 2010, 58, 9083–9091. [CrossRef]
- 244. Lamanna, M.; Morales, N.J.; García, N.L.; Goyanes, S. Development and characterization of starch nanoparticles by gamma radiation: Potential application as starch matrix filler. *Carbohydr. Polym.* **2013**, *97*, 90–97. [CrossRef] [PubMed]
- Zhu, J.; Li, L.; Chen, L.; Li, X. Study on supramolecular structural changes of ultrasonic treated potato starch granules. *Food Hydrocoll.* 2012, 29, 116–122. [CrossRef]
- 246. Boufi, S.; Haaj, S.B.; Magnin, A.; Pignon, F.; Impéror-Clerc, M.; Mortha, G. Ultrasonic assisted production of starch nanoparticles: Structural characterization and mechanism of disintegration. *Ultrason. Sonochem.* **2018**, *41*, 327–336. [CrossRef]

- 247. Grieser, F.; Ashokkumar, M.; Sostaric, J.Z. Sonochemistry and sonoluminescence in colloidal systems. In *Sonochemistry and Sonoluminescence*; Springer: Berlin/Heidelberg, Germany, 1999; pp. 345–362.
- 248. Kim, J.-Y.; Lim, S.-T. Preparation of nano-sized starch particles by complex formation with n-butanol. *Carbohydr. Polym.* **2009**, *76*, 110–116. [CrossRef]
- 249. Chin, S.F.; Azman, A.; Pang, S.C. Size controlled synthesis of starch nanoparticles by a microemulsion method. *J. Nanomater.* 2014, 2014, 9. [CrossRef]
- 250. Dong, Y.; Chang, Y.; Wang, Q.; Tong, J.; Zhou, J. Effect of operating conditions on size and morphology of amylose nanoparticles prepared by precipitation. *Starch-Stärke* **2015**, *67*, 365–372. [CrossRef]
- Qin, Y.; Liu, C.; Jiang, S.; Xiong, L.; Sun, Q. Characterization of starch nanoparticles prepared by nanoprecipitation: Influence of amylose content and starch type. *Ind. Crops Prod.* 2016, 87, 182–190. [CrossRef]
- Kim, H.-Y.; Han, J.-A.; Kweon, D.-K.; Park, J.-D.; Lim, S.-T. Effect of ultrasonic treatments on nanoparticle preparation of acid-hydrolyzed waxy maize starch. *Carbohydr. Polym.* 2013, 93, 582–588. [CrossRef]
- Chen, Y.; Cao, X.; Chang, P.R.; Huneault, M.A. Comparative study on the films of poly (vinyl alcohol)/pea starch nanocrystals and poly (vinyl alcohol)/native pea starch. *Carbohydr. Polym.* 2008, 73, 8–17. [CrossRef]
- Ma, X.; Jian, R.; Chang, P.R.; Yu, J. Fabrication and characterization of citric acid-modified starch nanoparticles/plasticized-starch composites. *Biomacromolecules* 2008, 9, 3314–3320. [CrossRef]
- 255. Tan, Y.; Xu, K.; Li, L.; Liu, C.; Song, C.; Wang, P. Fabrication of size-controlled starch-based nanospheres by nanoprecipitation. *ACS Appl. Mater. Interfaces* **2009**, *1*, 956–959. [CrossRef]
- Tay, S.H.; Pang, S.C.; Chin, S.F. A facile approach for controlled synthesis of hydrophilic starch-based nanoparticles from native sago starch. *Starch-Stärke* 2012, 64, 984–990. [CrossRef]
- 257. Angellier, H.; Choisnard, L.; Molina-Boisseau, S.; Ozil, P.; Dufresne, A. Optimization of the preparation of aqueous suspensions of waxy maize starch nanocrystals using a response surface methodology. *Biomacromolecules* 2004, *5*, 1545–1551. [CrossRef] [PubMed]
- Dufresne, A.; Cavaille, J.-Y.; Helbert, W. New nanocomposite materials: Microcrystalline starch reinforced thermoplastic. Macromolecules 1996, 29, 7624–7626. [CrossRef]
- Wang, Y.; Khan, A.; Liu, Y.; Feng, J.; Dai, L.; Wang, G.; Alam, N.; Tong, L.; Ni, Y. Chitosan oligosaccharide-based dual pH responsive nano-micelles for targeted delivery of hydrophobic drugs. *Carbohydr. Polym.* 2019, 223, 115061. [CrossRef] [PubMed]
- 260. Liu, J.; Ai, X.; Zhang, H.; Zhuo, W.; Mi, P. Polymeric micelles with endosome escape and redox-responsive functions for enhanced intracellular drug delivery. *J. Biomed. Nanotechnol.* **2019**, *15*, 373–381. [CrossRef]
- Liang, T.; Hou, J.; Qu, M.; Zhao, M.; Raj, I. High-viscosity α-starch nanogel particles to enhance oil recovery. *RSC Adv.* 2020, 10, 8275–8285. [CrossRef]
- 262. Movahedi, M.; Asefnejad, A.; Rafienia, M.; Khorasani, M.T. Potential of novel electrospun core-shell structured polyurethane/starch (hyaluronic acid) nanofibers for skin tissue engineering: In vitro and in vivo evaluation. *Int. J. Biol. Macromol.* 2020, 146, 627–637. [CrossRef]
- 263. Huang, Y.; Liu, M.; Gao, C.; Yang, J.; Zhang, X.; Zhang, X.; Liu, Z. Ultra-small and innocuous cationic starch nanospheres: Preparation, characterization and drug delivery study. *Int. J. Biol. Macromol.* **2013**, *58*, 231–239. [CrossRef]
- Zhou, G.; Luo, Z.; Fu, X. Preparation and characterization of starch nanoparticles in ionic liquid-in-oil microemulsions system. *Ind. Crops Prod.* 2014, 52, 105–110. [CrossRef]
- 265. Zhang, F.; Pei, X.; Zhai, K.; Wang, C.; Bai, Y.; Zhang, B.; Wang, Y.; Tan, Y.; Xu, K.; Wang, P. Starch-based nanospheres modified filter paper for o/w emulsions separation and contaminants removal. *Int. J. Biol. Macromol.* **2020**, *162*, 1118–1126. [CrossRef]
- 266. Shabana, S.; Prasansha, R.; Kalinina, I.; Potoroko, I.; Bagale, U.; Shirish, S.H. Ultrasound assisted acid hydrolyzed structure modification and loading of antioxidants on potato starch nanoparticles. *Ultrason. Sonochem.* 2019, *51*, 444–450. [CrossRef]
- 267. Ji, N.; Qin, Y.; Li, M.; Xiong, L.; Qiu, L.; Bian, X.; Sun, Q. Fabrication and characterization of starch nanohydrogels via reverse emulsification and internal gelation. *J. Agric. Food Chem.* **2018**, *66*, 9326–9334. [CrossRef]
- 268. Sharma, G.; Naushad, M.; Kumar, A.; Rana, S.; Sharma, S.; Bhatnagar, A.; Stadler, F.J.; Ghfar, A.A.; Khan, M.R. Efficient removal of coomassie brilliant blue R-250 dye using starch/poly (alginic acid-cl-acrylamide) nanohydrogel. *Process Saf. Environ. Prot.* 2017, 109, 301–310. [CrossRef]
- 269. Li, W.; Nie, J.; Hu, R.; Zhao, R.; Zhu, W.; Chen, X.; Li, D.; Wang, L.; Hu, L. A nanogel sensor for colorimetric fluorescence measurement of ionizing radiation doses. *Chem. Commun.* 2019, *55*, 9614–9617. [CrossRef] [PubMed]
- Noh, G.J.; Lim, S.A.; Lee, E.S. pH-responsive squeezing polysaccharidic nanogels for efficient docetaxel delivery. *Polym. Adv. Technol.* 2019, 30, 2067–2074. [CrossRef]
- 271. Lv, H.; Cui, S.; Zhang, H.; Pei, X.; Gao, Z.; Hu, J.; Zhou, Y.; Liu, Y. Crosslinked starch nanofibers with high mechanical strength and excellent water resistance for biomedical applications. *Biomed. Mater.* **2020**, *15*, 025007. [CrossRef]
- 272. Wang, W.; Jin, X.; Zhu, Y.; Zhu, C.; Yang, J.; Wang, H.; Lin, T. Effect of vapor-phase glutaraldehyde crosslinking on electrospun starch fibers. *Carbohydr. Polym.* 2016, 140, 356–361. [CrossRef] [PubMed]
- 273. Komur, B.; Bayrak, F.; Ekren, N.; Eroglu, M.; Oktar, F.N.; Sinirlioglu, Z.; Yucel, S.; Guler, O.; Gunduz, O. Starch/PCL composite nanofibers by co-axial electrospinning technique for biomedical applications. *Biomed. Eng. Online* 2017, 16, 40. [CrossRef] [PubMed]

- Wu, D.; Samanta, A.; Srivastava, R.K.; Hakkarainen, M. Starch-Derived Nanographene Oxide Paves the Way for Electrospinnable and Bioactive Starch Scaffolds for Bone Tissue Engineering. *Biomacromolecules* 2017, 18, 1582–1591. [CrossRef]
- Wang, X.; Liu, Z.; Huang, L. pH and thermo dual-responsive starch-g-P(DEAEMA-co-PEGMA): Synthesis via SET-LRP, selfassembly and drug release behaviors. *React. Funct. Polym.* 2019, 141, 165–171. [CrossRef]
- 276. Liu, W.; Li, Y.; Goff, H.D.; Nsor-Atindana, J.; Ma, J.; Zhong, F. Interfacial activity and self-assembly behavior of dissolved and granular octenyl succinate anhydride starches. *Langmuir* **2019**, *35*, 4702–4709. [CrossRef]
- 277. Wen, N.; Lü, S.; Xu, X.; Ning, P.; Wang, Z.; Zhang, Z.; Gao, C.; Liu, Y.; Liu, M. A polysaccharide-based micelle-hydrogel synergistic therapy system for diabetes and vascular diabetes complications treatment. *Mater. Sci. Eng. C* 2019, 100, 94–103. [CrossRef] [PubMed]
- Ying, X.; Shan, C.; Jiang, K.; Chen, Z.; Du, Y. Intracellular pH-sensitive delivery CaCO<sub>3</sub> nanoparticles templated by hydrophobic modified starch micelles. *RSC Adv.* 2014, 4, 10841–10844. [CrossRef]
- González-Seligra, P.; Guz, L.; Ochoa-Yepes, O.; Goyanes, S.; Famá, L. Influence of extrusion process conditions on starch film morphology. LWT 2017, 84, 520–528. [CrossRef]
- Cheng, Y.; Sun, C.; Zhai, X.; Zhang, R.; Zhang, S.; Sun, C.; Wang, W.; Hou, H. Effect of lipids with different physical state on the physicochemical properties of starch/gelatin edible films prepared by extrusion blowing. *Int. J. Biol. Macromol.* 2021, 185, 1005–1014. [CrossRef] [PubMed]
- 281. Sagar, A.D.; Merrill, E.W. Starch fragmentation during extrusion processing. Polymer 1995, 36, 1883–1886. [CrossRef]
- 282. Colonna, P.; Doublier, J.; Melcion, J.; De Monredon, F.; Mercier, C. Extrusion cooking and drum drying of wheat starch. *Cereal Chem.* **1984**, *61*, 538–554.
- Funke, U.; Bergthaller, W.; Lindhauer, M. Processing and characterization of biodegradable products based on starch. *Polym. Degrad. Stab.* 1998, 59, 293–296. [CrossRef]
- Gao, W.; Zhu, J.; Kang, X.; Wang, B.; Liu, P.; Cui, B.; Abd El-Aty, A. Development and characterization of starch films prepared by extrusion blowing: The synergistic plasticizing effect of water and glycerol. LWT 2021, 148, 111820. [CrossRef]
- Liu, H.; Xie, F.; Chen, L.; Yu, L.; Dean, K.; Bateman, S. Thermal Behaviour of High Amylose Cornstarch Studied by DSC. Int. J. Food Eng. 2005, 1, 1–6. [CrossRef]
- Rindlav-Westling, A.s.; Stading, M.; Hermansson, A.-M.; Gatenholm, P. Structure, mechanical and barrier properties of amylose and amylopectin films. *Carbohydr. Polym.* 1998, 36, 217–224. [CrossRef]
- Zhou, S.; Zhai, X.; Zhang, R.; Wang, W.; Lim, L.-T.; Hou, H. High-Throughput Fabrication of Antibacterial Starch/PBAT/AgNPs@SiO<sub>2</sub> Films for Food Packaging. *Nanomaterials* 2021, 11, 3062. [CrossRef]
- Ceballos, R.L.; Ochoa-Yepes, O.; Goyanes, S.; Bernal, C.; Famá, L. Effect of yerba mate extract on the performance of starch films obtained by extrusion and compression molding as active and smart packaging. *Carbohydr. Polym.* 2020, 244, 116495. [CrossRef]
   Mittal, V. *Polymer Nanocomposite Foams*; CRC Press/Taylor & Francis: Boca Raton, FL, USA, 2014.
- 290. Martins, P.C.; Gutkoski, L.C.; Martins, V.G. Impact of acid hydrolysis and esterification process in rice and potato starch properties. *Int. J. Biol. Macromol.* **2018**, *120*, 959–965. [CrossRef]
- Kaewtatip, K.; Poungroi, M.; Holló, B.; Mészáros Szécsényi, K. Effects of starch types on the properties of baked starch foams. J. Therm. Anal. Calorim. 2014, 115, 833–840. [CrossRef]
- 292. Vargas-Torres, A.; Palma-Rodriguez, H.M.; Berrios, J.D.J.; Glenn, G.; Salgado-Delgado, R.; Olarte-Paredes, A.; Prieto-Mendez, J.; Hernandez-Uribe, J.P. Biodegradable baked foam made with chayotextle starch mixed with plantain flour and wood fiber. J. Appl. Polym. Sci. 2017, 134, 45565. [CrossRef]
- 293. Chauvet, M.; Sauceau, M.; Baillon, F.; Fages, J. Blending and foaming thermoplastic starch with poly (lactic acid) by CO<sub>2</sub>-aided hot melt extrusion. *J. Appl. Polym. Sci.* 2021, 138, 50150. [CrossRef]
- Cheng, X.-H.; Wang, K.; Cheng, N.-Q.; Mi, S.-Y.; Sun, L.-S.; Yeh, J.-T. The control of expansion ratios and cellular structure of supercritical CO<sub>2</sub>-aid thermoplastic starch foams using crosslinking agents and nano-silica particles. *J. Polym. Res.* 2021, 28, 303. [CrossRef]
- 295. Amirreza, Z.; Mohammad, F.; Sajad, R. Microstructural and Physical Properties of Thermoplastic Corn Starch/Polystyrene Blend Foams Affected by Different Contents and Combinations of Plasticizers. *J. Polym. Environ.* 2021; *in press.* [CrossRef]
- 296. Viana, E.B.M.; Oliveira, N.L.; Ribeiro, J.S.; Almeida, M.F.; Souza, C.C.E.; Resende, J.V.; Santos, L.S.; Veloso, C.M. Development of starch-based bioplastics of green plantain banana (*Musa paradisiaca* L.) modified with heat-moisture treatment (HMT). *Food Packag. Shelf Life* **2022**, *31*, 100776. [CrossRef]
- 297. Cheng, M.; Cui, Y.; Yan, X.; Zhang, R.; Wang, J.; Wang, X. Effect of dual-modified cassava starches on intelligent packaging films containing red cabbage extracts. *Food Hydrocoll.* **2022**, *124*, 107225. [CrossRef]
- Reneker, D.H.; Kataphinan, W.; Theron, A.; Zussman, E.; Yarin, A.L. Nanofiber garlands of polycaprolactone by electrospinning. *Polymer* 2002, 43, 6785–6794. [CrossRef]
- Sutjarittangtham, K.; Jaiturong, P.; Intatha, U.; Pengpat, K.; Eitssayeam, S.; Sirithunyalug, J. Fabrication of natural tapioca starch fibers by a modified electrospinning technique. *Chiang Mai J. Sci.* 2014, 41, 213–223.
- 300. Kong, L.; Ziegler, G.R. Fabrication of pure starch fibers by electrospinning. Food Hydrocoll. 2014, 36, 20–25. [CrossRef]
- Fonseca, L.M.; de Oliveira, J.P.; de Oliveira, P.D.; da Rosa Zavareze, E.; Dias, A.R.G.; Lim, L.-T. Electrospinning of native and anionic corn starch fibers with different amylose contents. *Food Res. Int.* 2019, *116*, 1318–1326. [CrossRef]

- William, A.C.; Efrén, M.P.; Yesid, G.-P.E.; Ricardo, V.-G. Comparative Study of Starch Fibers Obtained by Electro-spinning of Indigenous, Commercial and Cationic Potato Starch. J. Nat. Fibers 2020, 17, 809–819. [CrossRef]
- Raghavan, B.; Soto, H.; Lozano, K. Fabrication of Melt Spun Polypropylene Nanofibers by Forcespinning. J. Eng. Fibers Fabr. 2013, 8, 155892501300800106. [CrossRef]
- Del Ángel-Sánchez, K.; Ulloa-Castillo, N.A.; Segura-Cárdenas, E.; Martinez-Romero, O.; Elías-Zuñiga, A. Design, fabrication, and characterization of polycaprolactone (PCL)-TiO<sub>2</sub>-collagenase nanofiber mesh scaffolds by Forcespinning. *MRS Commun.* 2019, 9, 390–397. [CrossRef]
- Li, X.; Chen, H.; Yang, B. Centrifugally spun starch-based fibers from amylopectin rich starches. *Carbohydr. Polym.* 2016, 137, 459–465. [CrossRef] [PubMed]
- Li, X.; Lu, Y.; Hou, T.; Zhou, J.; Yang, B. Centrifugally spun ultrafine starch/PEO fibres as release formulation for poorly water-soluble drugs. *Micro Nano Lett.* 2018, 13, 1688–1692. [CrossRef]
- Cui, Y.; Li, C.; Guo, Y.; Liu, X.; Zhu, F.; Liu, Z.; Liu, X.; Yang, F. Rheological & 3D printing properties of potato starch composite gels. J. Food Eng. 2022, 313, 110756. [CrossRef]
- 308. Leaw, Z.E.; Kong, I.; Pui, L.P. 3D printed corn starch–Gelatin film with glycerol and hawthorn berry (*Crataegus pinnatifida*) extract. J. Food Processing Preserv. 2021, 45, e15752. [CrossRef]
- 309. Gutiérrez, T.J.; Valencia, G.A. Reactive extrusion-processed native and phosphated starch-based food packaging films governed by the hierarchical structure. *Int. J. Biol. Macromol.* **2021**, 172, 439–451. [CrossRef]
- Bai, J.; Pei, H.; Zhou, X.; Xie, X. Reactive compatibilization and properties of low-cost and high-performance PBAT/thermoplastic starch blends. *Eur. Polym. J.* 2021, 143, 110198. [CrossRef]
- 311. Da Costa, J.C.M.; Miki, K.S.L.; da Silva Ramos, A.; Teixeira-Costa, B.E. Development of biodegradable films based on purple yam starch/chitosan for food application. *Heliyon* **2020**, *6*, e03718. [CrossRef]
- 312. Qin, Y.; Yun, D.; Xu, F.; Li, C.; Chen, D.; Liu, J. Impact of storage conditions on the structure and functionality of starch/polyvinyl alcohol films containing Lycium ruthenicum anthocyanins. *Food Packag. Shelf Life* **2021**, *29*, 100693. [CrossRef]
- 313. Abdillah, A.A.; Charles, A.L. Characterization of a natural biodegradable edible film obtained from arrowroot starch and iota-carrageenan and application in food packaging. *Int. J. Biol. Macromol.* **2021**, *191*, 618–626. [CrossRef]
- 314. Busolo, M.A.; Lagaron, J.M. Oxygen scavenging polyolefin nanocomposite films containing an iron modified kaolinite of interest in active food packaging applications. *Innov. Food Sci. Emerg. Technol.* **2012**, *16*, 211–217. [CrossRef]
- 315. Alam, A.U.; Rathi, P.; Beshai, H.; Sarabha, G.K.; Deen, M.J. Fruit quality monitoring with smart packaging. *Sensors* **2021**, *21*, 1509. [CrossRef] [PubMed]
- Terry, L.A.; Ilkenhans, T.; Poulston, S.; Rowsell, L.; Smith, A.W. Development of new palladium-promoted ethylene scavenger. Postharvest Biol. Technol. 2007, 45, 214–220. [CrossRef]
- 317. Smith, A.W.; Poulston, S.; Rowsell, L.; Terry, L.A.; Anderson, J.A. A new palladium-based ethylene scavenger to control ethylene-induced ripening of climacteric fruit. *Platin. Met. Rev.* **2009**, *53*, 112–122. [CrossRef]
- 318. Wills, R.; Warton, M. Efficacy of potassium permanganate impregnated into alumina beads to reduce atmospheric ethylene. *J. Am. Soc. Hortic. Sci.* 2004, 129, 433–438. [CrossRef]
- Jedermann, R.; Praeger, U.; Geyer, M.; Lang, W. Remote quality monitoring in the banana chain. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 2014, 372, 20130303. [CrossRef]
- 320. Mohan, C.; Ravishankar, C. Active and intelligent packaging systems—Application in seafood. *World J. Aquac. Res. Dev.* 2019, 1, 10–16.
- 321. Panrong, T.; Karbowiak, T.; Harnkarnsujarit, N. Thermoplastic starch and green tea blends with LLDPE films for active packaging of meat and oil-based products. *Food Packag. Shelf Life* **2019**, *21*, 100331. [CrossRef]
- Piñeros-Hernandez, D.; Medina-Jaramillo, C.; López-Córdoba, A.; Goyanes, S. Edible cassava starch films carrying rosemary antioxidant extracts for potential use as active food packaging. *Food Hydrocoll.* 2017, 63, 488–495. [CrossRef]
- Zheng, L.; Liu, L.; Yu, J.; Shao, P. Novel trends and applications of natural pH-responsive indicator film in food packaging for improved quality monitoring. *Food Control* 2022, 134, 108769. [CrossRef]
- 324. Silva-Pereira, M.C.; Teixeira, J.A.; Pereira-Júnior, V.A.; Stefani, R. Chitosan/corn starch blend films with extract from Brassica oleraceae (red cabbage) as a visual indicator of fish deterioration. *LWT-Food Sci. Technol.* **2015**, *61*, 258–262. [CrossRef]
- 325. Andretta, R.; Luchese, C.L.; Tessaro, I.C.; Spada, J.C. Development and characterization of pH-indicator films based on cassava starch and blueberry residue by thermocompression. *Food Hydrocoll.* **2019**, *93*, 317–324. [CrossRef]
- 326. Koshy, R.R.; Koshy, J.T.; Mary, S.K.; Sadanandan, S.; Jisha, S.; Pothan, L.A. Preparation of pH sensitive film based on starch/carbon nano dots incorporating anthocyanin for monitoring spoilage of pork. *Food Control* **2021**, 126, 108039. [CrossRef]
- 327. Shapi'i, R.A.; Othman, S.H.; Nordin, N.; Basha, R.K.; Naim, M.N. Antimicrobial properties of starch films incorporated with chitosan nanoparticles: In vitro and in vivo evaluation. *Carbohydr. Polym.* **2020**, 230, 115602. [CrossRef]
- 328. Díaz-Galindo, E.P.; Nesic, A.; Bautista-Baños, S.; Dublan García, O.; Cabrera-Barjas, G. Corn-starch-based materials incorporated with cinnamon oil emulsion: Physico-chemical characterization and biological activity. *Foods* **2020**, *9*, 475. [CrossRef]
- 329. Yun, D.; Cai, H.; Liu, Y.; Xiao, L.; Song, J.; Liu, J. Development of active and intelligent films based on cassava starch and Chinese bayberry (*Myrica rubra* Sieb. et Zucc.) anthocyanins. *RSC Adv.* **2019**, *9*, 30905–30916. [CrossRef]

- 330. Jayakumar, A.; Heera, K.; Sumi, T.; Joseph, M.; Mathew, S.; Praveen, G.; Nair, I.C.; Radhakrishnan, E. Starch-PVA composite films with zinc-oxide nanoparticles and phytochemicals as intelligent pH sensing wraps for food packaging application. *Int. J. Biol. Macromol.* **2019**, *136*, 395–403. [CrossRef] [PubMed]
- 331. Mustafa, P.; Niazi, M.B.; Jahan, Z.; Samin, G.; Hussain, A.; Ahmed, T.; Naqvi, S.R. PVA/starch/propolis/anthocyanins rosemary extract composite films as active and intelligent food packaging materials. *J. Food Saf.* **2020**, *40*, e12725. [CrossRef]
- 332. Aghazadeh, M.; Karim, R.; Sultan, M.T.; Paykary, M.; Johnson, S.K.; Shekarforoush, E. Comparison of starch films and effect of different rice starch-based coating formulations on physical properties of walnut during storage time at accelerated temperature. *J. Food Process Eng.* 2018, 41, e12607. [CrossRef]
- 333. Oliveira, B.F.; Cruz, A.; Xe, F.; Alves, E. Cassava starch coatings for postharvest control of papaya anthracnose. *Phytopathol. Mediterr.* **2016**, *55*, 276–284.
- Zhang, R.; Wang, X.; Cheng, M. Preparation and characterization of potato starch film with various size of nano-SiO<sub>2</sub>. *Polymers* 2018, 10, 1172. [CrossRef] [PubMed]
- 335. Castillo, L.A.; Farenzena, S.; Pintos, E.; Rodríguez, M.S.; Villar, M.A.; García, M.A.; López, O.V. Active films based on thermoplastic corn starch and chitosan oligomer for food packaging applications. *Food Packag. Shelf Life* 2017, 14, 128–136. [CrossRef]
- Mali, S.; Grossmann, M.V.E. Effects of Yam Starch Films on Storability and Quality of Fresh Strawberries (*Fragaria ananassa*). J. Agric. Food Chem. 2003, 51, 7005–7011. [CrossRef]