

Review



A Comprehensive Study on Starch Nanoparticle Potential as a Reinforcing Material in Bioplastic

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Abstract: Starch can be found in the stems, roots, fruits, and seeds of plants such as sweet potato, cassava, corn, potato, and many more. In addition to its original form, starch can be modified by reducing its size. Starch nanoparticles have a small size and large active surface area, making them suitable for use as fillers or as a reinforcing material in bioplastics. The aim of reinforcing material is to improve the characteristics of bioplastics. This literature study aims to provide in-depth information on the potential use of starch nanoparticles as a reinforcing material in bioplastic packaging. This study also reviews starch size reduction methods including acid hydrolysis, nanoprecipitation, milling, and others; characteristics of the nano-starch particle; and methods to produce bioplastic and its characteristics. The use of starch nanoparticles as a reinforcing material can increase tensile strength, reduce water vapor and oxygen permeability, and increase the biodegradability of bioplastics. However, the use of starch nanoparticles as a reinforcing material for bioplastic packaging still encounters obstacles in its commercialization efforts, due to high production costs and ineffectiveness.



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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/). Keywords: starch; starch nanoparticle; reinforcing material; bioplastic; biodegradable; characteristics

1. Introduction

Conventional plastic made from petrochemicals has taken on significant importance in modern life [1–5]. The increasing use of plastic causes an increase in the amount of plastic waste, which has a bad impact, especially on the environment and ecosystem [5]. One alternative is to substitute plastic packagings for more environmentally friendly options, such as bioplastics [6–8] or green composites [9]. Bioplastic refers to plastics that are made from organic or bio-based materials, have the characteristics of being naturally biodegradable or biodegradable, are made of organic materials, or can be degraded naturally [10,11]. The bioplastic degradation process is carried out by natural microorganisms, such as bacteria, fungi, and algae. This process produces CO_2 gas, methane gas, water, and biomass without any toxic by-products [12,13].

However, in general, bioplastic products are brittle, have low melting temperatures, and have low mechanical strength [1,14,15]. Bioplastics are also prone to disintegration during storage or use, are not chemically resistant, and have high water and oxygen permeability [15,16]. Using reinforcing material or filler is one option to improve the properties of the bioplastic matrix. The purpose of reinforcing material is to improve the properties of the matrix, such as enhancing degradability [1,17], increasing mechanical properties [18], and decreasing oxygen and water vapor permeability [13,19].

The basic material commonly used for the manufacture of reinforcing materials in bioplastics is starch. Starch is a polysaccharide derivative compound in the form of granules and is used by plants as an energy source. Starch granules have a semi-crystalline structure and are composed of amylose and amylopectin, which are complex carbohydrate polymers [20–22]. Amylose has a straight chain, while amylopectin has a branched chain [23]. In its use, starch can be used in its original form or can be modified beforehand for better characteristics, or as desired [24,25]. In its application, starch with high amylose content will produce products with higher water absorption [26,27]. Starch with high amylose content will also produce a stiffer gel structure. The ratio of amylose and amylopectin affects texture, solubility, viscosity, stability, gelatinization, moisture retention, retrogradation, and syneresis. These criteria affect the application and characteristics of the resulting product [28,29]. Starch is often modified to increase its functional properties and application [30–32].

One starch modification method is to reduce the size of starch particles to nanosize, which can be referred to as starch nanoparticles. Starch nanoparticles have at least 1 particle with a size of less than 300 nm and have a high active surface area [33]. Starch nanoparticles are spherical particles of nanosize that have varying crystallinity, and can also be completely amorphous [34]. In addition to the form of starch nanoparticles, there are also starch nanocrystals. Starch nanocrystals can be interpreted as a crystalline plate resulting from the removal of amorphous regions by hydrolysis. Starch nanocrystals have higher crystallinity when compared to starch nanoparticles [35].

Nowadays, the interest in research on bioplastics and reinforcing materials to produce bioplastics with better characteristics has increased. Starch is a promising resource because it is cheap, biodegradable, and abundant; thus, starch is promising in bioplastics and in reinforcing material production. This literature study is expected to provide in-depth information on the potential use of starch nanoparticles as reinforcing materials in bioplastics.

2. Preparation of Starch Nanoparticles for Bioplastic Reinforcing Material

There are two types of starch nanoparticle manufacturing methods, namely, topdown and bottom-up [36,37]. The top-down method focuses on reducing the granule size from bulk to micro- to nanosize, for example, by acid hydrolysis, ultrasonication, homogenization, gamma irradiation, and many more [38–41]. The bottom-up method focuses on the formation of nano-sized starch molecules from atoms under controlled conditions according to the laws of thermodynamics, such as nanoprecipitation and selfassembly methods [42–44]. Top-down methods are simple, require less cost, and are suitable for both laboratory and industrial scales. However, top-down methods are less effective for sources that have an irregular shape and an extremely small size. Bottom-up methods demand more money but require short production time and can generate less destructed starch [45]. Figure 1 illustrates starch nanoparticle production method with top-down and bottom-up approaches.

2.1. Physical Method

Examples of treatments that include physical methods are milling [46,47], highpressure homogenization [48–50], ultrasonication [51,52], and gamma irradiation [53,54]. The advantage of the physical method is that there is no use of chemicals or solvents, making it more environmentally friendly and simple. The time required in this method is also relatively shorter. The disadvantage of mechanical treatment is that it can cause damage to the crystalline structure of starch granules.

The physical method tends to result in starch nanoparticles with low crystallinity because the use of energy is very large, so the crystalline structure becomes weak [55]. This does not apply to gamma irradiation, as fragmentation by free radicals that occurs through gamma irradiation happens in the amorphous region, resulting in starch nanoparticles with relatively high crystallinity. Although gamma irradiation uses free radicals to destroy the chemical bonds of starch granules and starch particles become smaller, the free radicals here are not dangerous. Because they are easily soluble in water, the resulting starch



nanoparticles do not contain radical components [54]. On the other hand, other methods attack the crystalline region, thus resulting in starch nanoparticles with lower crystallinity.

Figure 1. Starch nanoparticle production method with top-down and bottom-up approaches.

Among the physical method for starch nanoparticle production, milling produces a larger size of starch nanoparticle. During milling, the reduction in starch granules to nanosize is obtained from the weight and speed of the grinding ball that continues to move and rotate. This movement will produce kinetic energy. This energy will be channeled to the sample, resulting in a reduction in the size sample [56]. It can be seen that corn starch processed by milling produces starch nanoparticles with a size of 245 nm [47], which is in line with another study [57].

The ultrasonication method is considered effective in reducing the size of starch. During ultrasonication, energy is transferred to the starch through a cavitation process, which is a condition where the microbubbles burst and spread in the solution suspension in the form of sound waves. This process involves high speed and generates shear forces that can break the covalent bonds of starch; thus, the starch particle size decreases [58]. Several studies have reported that the ultrasonication method produced cassava starch nanoparticles (35–65 nm) [59] and waxy maize starch nanoparticles (37 nm) [60], whereas high-pressure homogenization can produce sago starch nanoparticles (28.514 nm) [61]. The high pressures produce shear forces that can break starch hydrogen bonds, resulting in a reduction in the size of starch into nanoparticles [62].

2.2. Chemical and Enzymatic Method

Examples of chemical production methods for starch nanoparticles are acid hydrolysis [36,63,64] and nanoprecipitation [65–67]. The enzymatic method can be performed through enzymatic hydrolysis [68–70]. Acid and enzymatic hydrolysis use the same mechanism, which is that the area that will be attacked first is the amorphous region, then the acid and enzyme will attack the more crystalline region at a slower rate [17,71,72]. In nanoprecipitation, the starch is gelatinized first, then precipitated using an antisolvent such as ethanol. At the time of precipitation, starch chains will be broken, resulting in starch with a smaller size [73].

Chemical and enzymatic methods mostly result in starch nanoparticles with high crystallinity [74,75]. The difference between acid and enzymatic hydrolysis is that acid hydrolysis uses acid as a hydrolyzing agent, such as sulfuric acid (H_2SO_4) or chloride acid

(HCl) [76], while enzymatic hydrolysis uses hydrolase enzyme, such as pullulanase [77]. Although acid hydrolysis can produce high crystallinity starch nanoparticles, the time required for the production is far longer than enzymatic hydrolysis and nanoprecipitation. Most researchers that use acid hydrolysis require at least 5 days for hydrolysis [17,63,78], while enzymatic hydrolysis and nanoprecipitation require less than 1 day [43,70,79–82]. Potato starch nanoparticles which produce using hydrolysis have a higher crystallinity compared to enzymatic hydrolysis. Potato starch nanoparticles obtained by the enzymatic hydrolysis method have a crystallinity of 13.2% [80]. Meanwhile, potato starch nanoparticles obtained by acid hydrolysis and nanoprecipitation have a crystallinity of 42.2% and 44.1%, respectively [83].

Enzymatic hydrolysis tends to produce a higher yield of starch nanoparticle. A study showed potato starch nanoparticles with a manufacturing method using the pullulanase enzyme on elephant foot yam tuber starch, where the extraction yield obtained was 61.33% [84]. Another study also showed that the use of pullulanase enzymes in corn starch hydrolysis produced starch nanoparticles with a yield of 85% [79], while amadumbe starch nanoparticle produced through acid hydrolysis has a yield of 25% [85]. The differences in yield may be attributed to starch type in addition to hydrolysis type.

Regarding size, acid hydrolysis can produce starch nanoparticles with smaller sizes compared to nanoprecipitation. Putro et al. [86] have reported that the acid hydrolysis method produces potato starch nanoparticle with a smaller granule size than the nanoprecipitation method: 85.1 nm and 165.31 nm, respectively. This might be due to the native starch, with microparticle size being fragmented into smaller particles during acid hydrolysis; some of the amorphous parts were hydrolyzed into simple sugars, resulting in the formation of smaller nanoparticles. A previous study has reported that the granule size of starch nanoparticles also depends on amylose content and starch type; the smallest observed size of starch nanoparticles of potato, waxy maize, sweet potato, pea, tapioca, corn, and sweetcorn ranged from 15 to 50 nm, and the largest size observed was between 80 and 225 nm [82]. However, the size and the yield of the starch nanoparticles are influenced by the amylose content and starch crystallinity, where the starch with the low amylose content will produce starch nanoparticles with small size [73]. Waxy maize starch nanoparticles (1% amylose) produced through acid hydrolysis have a size of 47 nm, while high-amylose corn starch nanoparticles (70% amylose) produced with the same treatment have a size of 118 nm [87].

2.3. Combined Method

A combined method can be performed using two or more methods at one time of production. It is possible to combine chemical methods and chemical methods, physical methods, and physical methods, as well as chemical methods and physical methods. Examples of combined methods are the use of acid hydrolysis and ultrasonication, acid hydrolysis and precipitation, enzymatic hydrolysis and acid hydrolysis, and many more [88–92].

The use of the acid hydrolysis method with other methods, such as enzymatic hydrolysis, ultrasonication, and milling as a pre-treatment, can overcome the shortcomings of the acid hydrolysis method, namely, the long treatment time [83]. Such pre-treatment can increase the rate of hydrolysis because it means that the acid can reach and damage the amorphous region more quickly [73]. The study conducted by Zhou et al. [88] showed that the use of acid hydrolysis (hydrochloric acid vapor) combined with ultrasonication produces 80.5% waxy maize starch nanoparticles with the hydrolysis time of 1 h, whereas it usually takes more than 5 days for acid hydrolysis. Mango kernel nanoparticle starch produced by combining these two methods has a size of 24.4 nm with a yield of 24.4% [93]. Using the same method, procedure, and starch source, another study reported that the size of the mango kernel starch nanoparticle granule was 79 nm with a yield of 31.7% [94].

The use of ultrasonication before acid hydrolysis treatment can help acid molecules to reach the starch surface more quickly so that the required hydrolysis time is shorter [95]. The cavitation process that occurs during ultrasonication produces a shear force that has an

impact on the damage to the starch surface. The extraction yield obtained is also higher with high crystallinity [35]. The production of starch nanoparticles using several methods is presented in Table 1.

 Table 1. Starch nanoparticle production methods.

Starch Source	Method	Treatment	Results	Ref.
Cassava	Ultrasonication	Time: 30 min Frequency: 20 kHz Temperature: 25 °C	Particle diameter: 35–65 nm Yield: 12%	[59]
Corn	Milling	Media: water Milling speed: 3500 rpm Time: 90 min	Particle size: 245 nm	[47]
Corn	Extrusion	The ratio of starch: water: glycerol = 100:22:23 Storage temperature: 2 °C Storage time: 24 h Extrusion speed: 100–360 rpm Extrusion temperature: 55–110 °C	The higher the extrusion temperature, the smaller the particle size (160 nm)	[57]
Waxy maize	Ultrasonication	Temperature: 8 °C Frequency: 20 kHz Time: 75 min	Particle size: 37 nm	[60]
Cassava	Gamma irradiation	Dose: 20 kGy Speed: 14 kGy/h	Particle size: 31 nm	[54]
Sago	НРН	Media: aquadest Pressure: 250 MPa Time: in 1 h	Particle diameter: 28.514 nm	[61]
Amaranth	АН	Acid: H ₂ SO ₄ 3.16 M Temperature: 40 °C Time: 3, 5, and 10 days	Yield on day 3: 17% Particle size: 374 nm	[96]
Potato	ЕН	Enzyme: α-amylase Incubation time: 30 min Incubation temperature: of 60 °C	Yield: 29% Size: 301 nm	[80]
Potato	АН	Acid: H ₂ SO ₄ 3.16 M Homogenization speed: 200 rpm Temperature: 40 °C Time: 5 days	Diameter: 237.03 nm	[83]
Corn	EH	Enzyme: pullulanase Temperature: 58 °C Time: 8 h	Yield: >85%	[79]
Waxy maize	АН	Acid: HCl 2.2 N Temperature: 35 °C Time: 10 days	Size: 30–300 nm	[97]
Elephant foot yam	EH	Enzyme: pullulanase Temperature: 60 °C Time: 8 h	Yield: 61.33% Particle size: 198.14 nm	[84]
Waxy maize High-amylose maize	АН	Acid: H ₂ SO ₄ 3.16 M Temperature: 40 °C Time: 6 days	Particle size: 47 nm Shape: elliptical Particle size: 118 nm	[87]
Rice	АН	Acid: H ₂ SO ₄ 3 M Temperature: 40 °C Time: 5 days	Crystallinity: 13.3% Crystalline type: A	[98]

Starch Source	Method	Treatment	Results	Ref.
Amadumbe	АН	Acid: H ₂ SO ₄ 3.16 M Temperature: 40 °C Time: 5 days	Yield: 25% Particle size: 50–100 nm	[85]
Waxy maize	Self-assembly	Enzyme: pullulanase Incubation time: 8 h Incubation temperature: 4 °C	Particle size: 200–300 nm	[99]
High-amylose maize Pea Potato Corn Tapioca Sweet potato Waxy maize	NP	Solvent: ethanol Temperature: room temperature Time: 8 h	Particle size: 20–80 nm Particle size: 30–150 nm Particle size: 50–225 nm Particle size: 15–80 nm Particle size: 30–110 nm Particle size: 40–100 nm Particle size: 20–200 nm	[82]
Corn	AH + ultrasonication	Acid: H ₂ SO ₄ 3.16 M Hydrolysis time: 10 days Ultrasonication frequency: 40 kHz Ultrasonication time: 45 min Ultrasonication temperature: 40 °C	Yield: 22% Particle size: 109.9 nm	[100]
Таріоса	NP + sonication	Solvent: ethanol and aquadest Temperature: 22 °C Ultrasonication time: 60 min Ultrasonication frequency of 20 kHz	Particle size: 163 nm	[81]
Waxy maize	Milling + AH	Milling media: ethanol anhydrate Milling speed: 300 rpm Milling time: 15, 30, 45, 60, 75, and 90 min Milling temperature: 40 °C Acid: H ₂ SO ₄ 3.16 M Hydrolysis temperature: 40 °C Hydrolysis time: 5 days	The longer the hydrolysis time, the decrease in extraction yield and a reduction in particle size	[101]
Potato	NP	Solution: NaOH Tween (non-ionic surfactant) Solvent: ethanol Solution pH: 7	Diameter: 71.81 nm	[83]
Mango kernel	AH + sonication	Acid: HCl 3.16 M and H ₃ PO ₄ 3.16 M Incubation temperature: 40 °C Incubation time: 5 days Sonication was performed within 20 min with frequency of 450 W	Yield: 24.4% Particle size: 24.4 nm	[93]
Mango kernel Corn	AH + sonication	Acid: HCl 3.16 M and H ₃ PO ₄ 3.16 M Incubation temperature: 40 °C Incubation time: 5 days Sonication was performed within 20 min with frequency of 450 W	Yield: 31.7% Particle size: 79 nm Yield: 19.4% Particle size: 61.1 nm	[94]

 Table 1. Cont.

AH: acid hydrolysis; EH: enzymatic hydrolysis: HPH: high-pressure homogenization; H₂SO₄: sulfuric acid, HCl: hydrochloric acid, H₃PO₄: phosphoric acid, NaOH: sodium hydroxide; NP: nanoprecipitation.

3. Properties of Starch Nanoparticles

3.1. Amylose Content

Amylose content in starch can be analyzed using the iodine-binding method. When amylose meets iodine, it produces a blue color, while amylopectin reacts with iodine to produce a red–purple color that is not too bright [102]. Minakawa et al. [59] reported that yam starch nanoparticles produced by ultrasonication have higher blue value than corn and cassava starch nanoparticles produced using the same method. Higher blue value indicates a higher amylose content in starch.

Potato starch nanoparticles obtained through the nanoprecipitation method had the highest amylose content (21.39%) compared to the acid hydrolysis method (4.79%) and the combined acid hydrolysis method with ultrasonication (3.08%) [83]. In starch nanoparticles from the acid hydrolysis method, amylose content decreased. This is because the amorphous areas in starch granules are very sensitive to acid, so the amorphous areas can be hydrolyzed and leave crystalline regions [102]. Starch crystallinity also has a relation with amylose and amylopectin. Starch crystallinity is attributed to the packing of double helixes formed by amylopectin side chains; thus, starch with higher amylopectin tends to have higher relative crystallinity [87].

Furthermore, LeCorre et al. [87] have reported that amylose content plays a role in determining the particle size of starch nanoparticles, where starch with low amylose content tends to produce starch nanoparticles with smaller particle sizes. This is because amylose is considered to be able to inhibit the hydrolysis process so that hydrolysis becomes slower and the resulting particle size becomes larger.

3.2. Granule Morphology Shape and Size

Granule morphology and the size of starch nanoparticles were analyzed using SEM (scanning electron microscopy), TEM (transmission electron microscopy), or FE-SEM (fieldemission scanning electron microscopy) [95]. Granule morphology shape and the sizes of starch nanoparticles from various starch sources and production methods are presented in Table 2. A previous study by Hernández-Jaimes et al. [103] reported that acid hydrolysis treatment caused changes in the shape and size of native starch granules and presented erosions and fractures on the granule surface. The longer the hydrolysis process, the higher the deformation on the surface. As the hydrolysis time increases, deeper surface erosion occurs, which eventually leads to the fragmentation of some starch granules. The presence of some small remnant granules after 15 days was observed. The number of nanoparticles increases with longer acid hydrolysis times.

Table 2. Granule morphology shape and size of starch nanoparticles from various starch sources and production methods.

Starch Source	Method	Granule Morphology Shape	Particle Size (nm)	Ref.
Banana	NP	Irregular	135	[103]
Waxy maize	Milling + AH	Round to irregular	67.2	[101]
Potato	AH AH + ultrasonication	Elliptic-polyhedric	237.03 153.63	[83]
	NP	Emplie polynearie	71.81	[00]
Waxy rice	AH	Irregular	20-420	[97]
Waxy maize Potato	Cold plasma + ultrasonication	Round and polyhedral	342 336	[104]

Starch Source	Method	Granule Morphology Shape	Particle Size (nm)	Ref.	
Tanioca	NP + sonication	Round	163	[91]	
Taploca	NP	Round	219	[01]	
Corn	AH + ultrasonication	Grape-like and parallelepiped	83.9	[100]	
Corn			36–68		
Cassava	Ultrasonication	Round	35–65	[59]	
Yam			8–32		
Amaranth		D	374	[0/]	
Waxy maize	AH	Parallelepiped	322	[96]	
Potato	Ultrasonication	Round	74.8	[105]	
Waxy maize	Self-assembly	Spherical	200–300	[99]	
Corn	Corn Waxy maize		82	[()]	
Waxy maize			297	[60]	
	АН	Spherical	58		
Waxy maize	Ultrasonication	Ellipsoidal	37	[34]	
Amadumbe	AH	Parallelepiped	50-100	[85]	
Mango kernel	AH + sonication	Round	67.1	[93]	
Cassava		NR	31	[[] 4]	
Waxy maize	Gamma irradiation	NR	41	[34]	
Mango kernel		Spherical	79	[0,1]	
Corn	AH + sonication	Spherical	61.1	[94]	
Cassava	Gamma irradiation	NR	50-100	[106]	
High-amylose maize			20-80		
Pea			30-150		
Potato			50-225		
Corn	NP	Round and oval	15-80	[82]	
Таріоса			30-110		
Sweet potato			40-100		
Waxy maize			20-200		
Potato	C.1(December 201	9–40	[107]	
Waxy maize	Self-assembly	Kound to irregular	50-120	[107]	

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Table 2. Cont.
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AH: acid hydrolysis; NP: nanoprecipitation; NR: not reported.

Furthermore, Minakawa et al. [59] reported that ultrasonic treatment causes granule surfaces to crack and erode progressively, as observed by SEM. Some smaller particles are released with different morphology than their native starch granule. This result was in agreement with another study [60], which reported that the ultrasonication method reduces the granule size of waxy maize starch from 2–15 μ m to 20–200 nm. The surface of the starch granules appears to be broken down and eroded progressively with increasing ultrasonication time.

Crystallinity can be interpreted as a comparison between the mass of the crystalline region with the mass of starch nanoparticles as a whole [73]. Starch crystalline structure can be observed using XRD (X-ray diffractograms). The crystalline type of starch nanoparticle can be influenced by the variety or cultivars of the starch source. Banana starch from different cultivars shows different types of crystalline [108].

Starch crystallinity has a relationship with the double-helix structure of the amylopectin chain, so starches with high amylopectin content tend to have high crystallinity compared to starches with high amylose content [87]. Starch nanoparticles of waxy maize with the acid hydrolysis method have a crystallinity of 69%. Meanwhile, the ultrasonication production method obtained 0% crystallinity [34]. Tapioca starch has a crystallinity of 25.12%, which decreased to 12.53% after the nanoprecipitation process and decreased to 6.49% after the nanoprecipitation + ultrasonication process [81]. This is due to the ultrasonication and nanoprecipitation processes attacking the crystallinity [59,81]. Meanwhile, acid and enzymatic hydrolysis attack the amorphous region first; hence, the starch nanoparticles produced from acid and enzymatic hydrolysis have higher crystallinity [79,96,103]. Plantain starch nanoparticles obtained from acid hydrolysis have a relative crystallinity of 90% [103]. The relative crystallinity and crystallinity patterns of starch nanoparticles from various starch sources and production methods are shown in Table 3.

Table 3. The relative crystallinity and crystallinity patterns of starch nanoparticles from various starch sources and production methods.

Starch Source	Method	Relative Crystallinity (%)	Crystalline Type	Ref.	
Plantain	AH	90	Туре-В	[103]	
Waxy maize	Milling + AH	49	NR	[101]	
	AH	42.2	Туре-В		
Potato	AH + ultrasonication	61.3	Туре-В	[83]	
	NP	44.1	Type-V		
Potato		17.5	NR		
Maize	EH	21.3	NR	[80]	
Cassava		13.2	NR		
Waxy rice	AH	NR	Type-A	[97]	
Waxy maize	Cold plasma +	43	Туре-А	[104]	
Potato	ultrasonication	29.1	Type-B		
Taniaca	NP + sonication 15.21		Type-V	[01]	
Tapioca	NP	12.53	Type-V	[01]	
Corn	AH + ultrasonication	36.6	NR	[100]	
Corn		8	Type-A		
Cassava	Ultrasonication	0	Type-V	[59]	
Yam		9	Туре-В		
Amaranth	A T T	35	Type-A	[06]	
Waxy maize	АН	36.5	Type-A	[90]	
Potato	Ultrasonication	NR	Type-V	[105]	
Waxy maize	EH	55.41	Type B+V	[79]	
Corn Waxy maize	Ultrasonication	NR NR	Type-V Type-V	[60]	

Starch Source	Method	Relative Crystallinity (%)	Crystalline Type	Ref.
Waxy maize	AH Ultrasonication	69 0	Type-A NR	[34]
Rice	AH	13.3	Type-A	[98]
Amadumbe	AH	NR	Type-A	[85]
Mango kernel	AH + sonication	62.2	Type-A	[93]
Mango kernel Corn	AH + sonication	NR NR	Туре-А Туре-А	[94]
Taro	EH	NR	Type B+V	[109]
High-amylose maize Pea Potato Corn Tapioca Sweet potato Waxy maize	NP	39.8 31.5 26.3 23.2 19.3 20.7 7.1	Type-V	[82]
Potato Waxy maize	Self-assembly	54.31 55.41	Туре-В	[107]

Table 3. Cont.

AH: acid hydrolysis; EH: enzymatic hydrolysis; NP: nanoprecipitation; NR: not reported.

3.4. Thermal Properties

Thermal characteristics can be analyzed using DSC (differential scanning calorimetry) and TGA (thermogravimetric analysis). The parameters observed include T_o (onset temperature), T_c (endset temperature), T_p (peak temperature), T_c-T_o (melting temperature range), and Δ H (enthalpy change) [70]. Starch nanoparticles have lower thermal stability when compared to native starch. This is due to a decrease in the molecular weight of the starch nanoparticles [79]. The ultrasonication and nanoprecipitation processes can reduce the thermal stability of starch nanoparticles compared to native starch. Native tapicca starch has T_o, T_p, T_c, and Δ H values of 57.07 °C, 66.33 °C, 73.73 °C, and 9.84 J/g, respectively. The nanoprecipitation + ultrasonication process reduces T_o, T_p, T_c, and Δ H by 40.77 °C, 50.39 °C, 63.8 °C, and 1.99 J/g, respectively [81]. A lower enthalpy indicates a poorer starch molecular structure [29]. The thermal properties of starch nanoparticles from various starch sources and production methods are presented in Table 4.

Table 4. Th	ermal pr	operties of s	starch nand	oparticles	from varie	ous starch	sources and	production	n methods
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Starch Source	Method	Т ₀ (°С)	Т _р (°С)	T _c (°C)	$T_c - T_o$ (°C)	AH (J/g)	Ref.
Plantain	AH	74.6	93.6	106.9	32.3	24.6	[103]
Waxy maize Potato	Cold plasma + ultrasonication	63.18 53.24	68.95 56.98	77.54 61.95	14.36 8.71	14.13 12.83	[104]
Таріоса	NP + sonication NP	52.88 40.77	60.15 55.14	70.42 67.08	23.03 20.7	6.61 4.64	[81]
Waxy rice	AH	62.68	68.62	77.95	15.27	3.3	[97]

Starch Source	Method	T ₀ (°C)	Т _р (°С)	Τ _c (° C)	Τ _c - Τ _o (° C)	AH (J/g)	Ref.
High-amylose maize		48.19	61.20	71.20	23.01	6.16	
Pea		46.51	60.42	73.47	26.96	4.57	
Potato		43.45	66.42	73.31	29.86	4.34	
Corn	NP	41.21	55.29	70.31	29.10	4.21	[82]
Tapioca		44.21	54.14	67.62	23.41	2.37	
Sweet potato		42.74	56.24	70.21	27.47	3.02	
Waxy maize		44.13	59.54	70.44	26.31	0.96	
Potato	Solf accombly	65.97	97.39	101.32	35.35	-5.34	[107]
Waxy maize	Self-assellibly	62.4	78.31	93.24	30.84	-10.17	[107]
Waxy maize	A T T	57.70	92.40	81.90	24.20	34.6	[(2]
Corn	AH	60.20	89.10	116.70	56.50	20.20	[63]

 Table 4. Cont.

AH: acid hydrolysis; NP: nanoprecipitation.

4. Definition and Preparation of Bioplastic with Starch Nanoparticles as Reinforcing Material

Bioplastic refers to plastics that are made from biomass or are bio-based, plastics that have the characteristics of being biodegradable, or plastics made from biomass that can be degraded naturally [10,110]. Examples of bio-based bioplastic packaging are bio-PE and bio-PET [111]; examples of biodegradable bioplastic packaging are PBS (polybutylene succinate), PCL (polycaprolactone), and PVA (polyvinyl alcohol); examples of bioplastics that have bio-based and biodegradable properties are PLA (polylactic acid), PHA (polyhydroxyalkanoate), and packaging with a mixture of starch, cellulose, or lignin [112–117].

The methods commonly used for the manufacture of bioplastic packaging are solution casting [98,118–120], injection molding [121,122], compression molding [123], and extrusion [124–126]. The casting method is very simple and inexpensive; thus, this method is suitable for use on a laboratory scale [127]. On the other hand, it also has drawbacks because it is not suitable for industrial scale [23]. In the manufacture of bioplastic packaging with a starch matrix, starch gelatinization is carried out first with or without a plasticizer. Subsequently, the mixture of starch and plasticizer was cooled to inhibit the gelatinization of the starch nanoparticle. The film solution is then poured into a mold and heated at a certain temperature and time. After cooling and molding, the film can be removed from the mold [98].

The injection molding method produces packaging with good characteristics with effective production costs, including in large-scale production. Before printing, the dough must first be made which is a mixture of matrix and plasticizer. The injection process is carried out using a piston injection molding machine [128]. The extrusion method is suitable for industrial-scale production and requires low production costs. However, the use of nanoparticles in the extrusion method can increase the tendency of nanoparticles to form aggregates; thus, extrusion may not be suitable for bioplastic manufacturing with a starch nanoparticle as the reinforcing material [16]. The steps in the production of bioplastic packaging using the extrusion method consist of mixing, extrusion, and die-cutting stages to obtain bioplastic samples with certain dimensions. The extrusion process is carried out using an extruder machine [124].

5. Characteristics of Bioplastic with Starch Nanoparticles as Reinforcing Material

This paper will discuss the mechanical properties, water vapor permeability, thermal properties, and biodegradability of bioplastic with various starch nanoparticles for reinforcement. All the literature used in discussing the characteristics below use casting as a bioplastic production method. A lot of researchers use the casting method because the casting method is the simplest and most inexpensive method, compared to other methods.

The characteristics of bioplastic with starch nanoparticle reinforcement will be influenced by filler concentration, filler–matrix interaction, and filler characteristics [129,130].

5.1. Mechanical Properties

Parameters tested include flexibility, strength, and stiffness of the bioplastic film. Mechanical characteristics can be analyzed using a TA (texture analyzer) [101] or using DMA (dynamic mechanical analysis) [131]. The effect of the use of reinforcing material on the strength of bioplastic packaging might be caused by the bond between the surface of the reinforcing material and the matrix, resulting in a stress distribution through the friction mechanism between the reinforcing material and the matrix to increase the strength of the bioplastic packaging [85]. The use of reinforcing materials causes the packaging structure to become denser and more compact, thus increasing the mechanical strength of bioplastics [109].

Piyada et al. [98] have reported a study on rice starch film with rice starch nanocrystals as a reinforcing material and and sorbitol as a plasticizer. As the reinforcing material composition increases, the flexibility of the bioplastic decreases, and the tensile strength increases. Bioplastic without reinforcing material has an elongation at a break of 53.46% and a tensile strength of 7.12 MPa. The use of 30% rice starch nanoparticle as a reinforcing material produces bioplastics with a flexibility of 2.48% and a tensile strength of 12.86 MPa. Another research [132] showed a similar trend, where the reinforcing material composition increased, the flexibility of the bioplastic decreased, and the tensile strength increased. Furthermore, addition of 10% starch nanoparticle as a reinforcing material decreased elongation at break from 1550% to 905% and increased tensile strength from 13.5 MPa to 19.9 MPa. The mechanical properties of bioplastics with various compositions are presented in Table 5.

Bioplastic Composition			Flongation at	Young Modulus	Tensile	
Matrix	Reinforcing Material	Plasticizer	Break (%E)	(MPa)	Strength (MPa)	Ref.
Polyurethane	Corn SNP 0% 5% 10% 20% 30%	-	29.8 44.6 67 61.1 70.3	NR	8.5 11.8 15.9 16.2 17.1	[95]
Cassava starch (4)	Cassava SNP (0) (0.5) (5) (10)	Glycerol (2.1)	NR	4.8 5 15.2 29.8	1 1.24 1.98 3.15	[19]
Sago starch	Sago SNP 0% 2% 4% 6% 8%	-	$ 1.24 \\ 1.5 \\ 1.62 \\ 1.67 \\ 1.58 $	2.314 2.87 3.21 2.532 2.444	2.469 2.902 3.578 2.669 2.546	[61]
Waterborne polyurethane	Pea SNP 0% 5% 10% 20% 30%	-	825 718 600 526 300	3 7 115 195 208	11.5 29 31 25 14	[133]

Table 5. Mechanical properties of bioplastics with various compositions.

Bi	oplastic Composition		Flongation at	Young Modulus	Tensile	
Matrix	Reinforcing Material	Plasticizer	Break (%E)	(MPa)	Strength (MPa)	Ref.
Polycaprolactone	Corn SNP 0% 2.25% 5% 10%	-	1550 1455 1410 905	274.8 310.7 333.6 339.3	13.5 17.7 19.5 19.9	[132]
Rice starch	Rice SNP 0% 5% 10% 15% 20% 25% 30%	Sorbitol 40%	53.46 34.76 28.75 17.12 8.89 2.51 2.48	NR	7.12 10.82 11.53 12.79 16.43 13.91 12.86	[98]
Potato starch	Amadumbe SNP 0% 2.5% 5% 10%	Glycerol	NR	NR	2.09 8.11 5.91 6.7	[85]
Amadumbe starch	Amadumbe SNP 0% 2.5% 5% 10%	Glycerol	NR	NR	2.4 3.89 3.37 2.08	[00]
Cross-linked cassava starch	Cassava SNP 0% 2% 4% 6% 8%	Glycerol	175.87 138.21 98.85 76.46 60	10 10.98 11.87 12.96 12.5	5.48 7 8.97 9.17 8.75	[134]
Corn starch	Corn SNP 0 2.5% 5% 7.5% 10%	Glycerol	770.5 746.3 997 1112.9 1462	10.95 9.32 11.95 12.12 15.87	20.34 20.98 9.86 9.35 2.85	[94]
Mango kernel starch	Mango kernel SNP 0% 2.5% 5% 7.5% 10%	Glycerol	659.1 793.8 1466.2 1899.4 1437	9.3 10.39 17.51 18.96 15.47	22.85 19.61 11.15 1.53 2.03	[די]
Pea starch	Potato SNP 0% 3% 6% 9% 12%	Glycerol 3 g	53.4 52.7 48.6 45 37	NR	8.8 11.5 15 9.8 9.5	[99]

Table 5. Cont.

Bio	oplastic Composition		Elemention at	Vour a Madulua	Toncilo	
Matrix	Reinforcing Material	Plasticizer	Break (%E)	(MPa)	Strength (MPa)	Ref.
Corn starch	Taro SNP 0% 0.5% 2% 5% 10% 15%	Glycerol 3 g	84.5 80 74.7 66.8 64.1 58	NR	1.1 1.53 1.74 2.51 2.87 2.28	[109]
Pea starch	Waxy maize SNP 0% 1% 3% 5% 7% 9%	Glycerol 3%	29.23 26.18 20.46 12.58 21.6 26.7	21.15 27.95 37.89 85.72 36.59 27.56	5.76 6.56 6.95 9.96 7.12 6.68	[135]
Soy protein isolate 0.25 g	Corn SNP 0% 2% 5% 10% 20% 40%	Glycerol 0.125 g	65.95 53.79 58.67 32.17 41.89 21.35	26.89 55.31 39.42 71.05 102.23 310.34	$ \begin{array}{c} 1.1 \\ 1.42 \\ 1.34 \\ 1.79 \\ 2.61 \\ 5.08 \\ \end{array} $	[136]
Carboxymethyl chitosan 5 g	Waxy maize SNP 0% 3% 6% 10% 15% 20% 30% 40%	Glycerol 2 g	180.24 180 160 148.79 137.68 115.47 97.36 62	NR	15.36 17 18.78 19.94 21.5 26.87 28.32 26.9	[137]
Pullulan	Waxy maize SNP 0% 3% 6% 10% 15% 20% 30% 40%	Sorbitol 30%	237 139 120 110 67 58 40 16	94 100 124 586 687 700 1004 1295	6 8 9.3 9.5 14 15.2 19.8 26.2	[138]
Waxy maize starch	Waxy maize SNP 0% 5% 10% 15%	Sorbitol 25%	63 57 58 41	17.2 36.6 38.3 46.2	0.38 0.99 1.37 1.59	[139]

Table 5. Cont.

NR: not reported; SNP: starch nanoparticle.

5.2. Water Vapor Permeability

The interaction of the reinforcing material and the matrix in bioplastic packaging forms a strong bond so that the water and air entry paths in the matrix molecules become torturous. This makes it difficult for air and water vapor to penetrate through the packaging film [61]. With a higher concentration of reinforcing material, the structure inside the package will become denser and the pores in the package will be smaller, making it difficult for water and air vapor to penetrate the packaging wall. However, there is also a maximum concentration at which the reinforcing material can work optimally [95]. No data have been found regarding the optimal composition for the use of starch nanoparticles as a reinforcement in bioplastics. This might be due to the optimal concentration of starch nanoparticles being highly dependent on the type of matrix.

The use of reinforcing material is effective in reducing water vapor and oxygen permeability. Bioplastic with a polyurethane matrix (PU) and a reinforcing material of corn starch nanoparticles has a water vapor permeability (WVP) of 3.17% without the use of reinforcing material, which decreases to 0.92% with the use of 30% reinforcing material. Oxygen permeability also decreased from 27.5% with 0% reinforcing material to 6.7% with 30% reinforcing material [95]. A previous study [137] showed that the maximum reinforcing material concentration in the bioplastic composition was 20%, where the matrix used was carboxymethyl chitosan and the reinforcing material used was waxy maize starch nanoparticles with a glycerol plasticizer. When the starch nanocrystal content was higher than 30%, they aggregated and the phase separated in the matrix. The water vapor permeability of bioplastic with various compositions is presented in Table 6.

Bioplastic Composition					
Matrix	Reinforcing Material	Plasticizer	Pa.m.h)	Ref.	
Sago starch	Sago SNP 0% 2% 4% 6% 8%	-	$\begin{array}{c} 12.08\times10^{-3}\\ 7.80\times10^{-3}\\ 6.81\times10^{-3}\\ 5.93\times10^{-3}\\ 6.42\times10^{-3} \end{array}$	[61]	
Starch rice	SNP rice 0% 5% 10% 15% 20%	Sorbitol 40%	$\begin{array}{c} 0.75\times 10^{-13}\\ 0.66\times 10^{-13}\\ 0.60\times 10^{-13}\\ 0.31\times 10^{-13}\\ 0.30\times 10^{-13} \end{array}$	[98]	
Potato starch	Amadumbe SNP 0% 2.5% 5% 10%	Glycerol	$\begin{array}{c} 1.8\times 10^{-5}\\ 1.6\times 10^{-5}\\ 1.5\times 10^{-5}\\ 1.5\times 10^{-5}\end{array}$	[85]	
Amadumbe starch	Amadumbe SNP 0% 2.5% 5% 10%	Glycerol	$\begin{array}{c} 2.3\times10^{-5}\\ 2.1\times10^{-5}\\ 2.0\times10^{-5}\\ 1.8\times10^{-5} \end{array}$	[00]	
Waxy maize starch	Waxy maize SNP 0% 2.5%	Glycerol 33%	1.37×10^{-6} 2.45×10^{-6}	[140]	

Table 6. Water vapor permeability of bioplastic with various compositions.

Bioplastic Composition			WIVE (~/		
Matrix	Reinforcing Material	Plasticizer	Pa.m.h)	Ref.	
Corn starch	Corn SNP 0% 2.5% 5% 7.5% 10%	Glycerol	$\begin{array}{c} 1.41 \times 10^{-6} \\ 1.25 \times 10^{-6} \\ 1.15 \times 10^{-6} \\ 1.11 \times 10^{-6} \\ 1.12 \times 10^{-6} \end{array}$	[94]	
Mango kernel starch	Mango kernel SNP 0% 2.5% 5% 7.5% 10%	Glycerol	$\begin{array}{c} 1.37 \times 10^{-6} \\ 1.35 \times 10^{-6} \\ 1.21 \times 10^{-6} \\ 1.08 \times 10^{-6} \\ 1.00 \times 10^{-6} \end{array}$	[74]	
Corn starch 7.5 g	Taro SNP 0% 0.5% 2% 5% 10% 15%	Glycerol 3 g	$\begin{array}{c} 2.74 \times 10^{-7} \\ 2.05 \times 10^{-7} \\ 1.83 \times 10^{-7} \\ 1.49 \times 10^{-7} \\ 1.20 \times 10^{-7} \\ 1.37 \times 10^{-7} \end{array}$	[109]	
Pea starch 5 g	Waxy maize SNP 0% 1% 3% 5% 7% 9%	Glycerol 1.5 g	$\begin{array}{c} 11.18\times 10^{-3}\\ 7.57\times 10^{-3}\\ 6.09\times 10^{-3}\\ 4.26\times 10^{-3}\\ 5.41\times 10^{-3}\\ 5.50\times 10^{-3} \end{array}$	[135]	
Soy protein isolate 0.25 g	Corn SNP 0% 5% 20% 40%	Glycerol 0.125 g	$\begin{array}{c} 4.3 \times 10^{-6} \\ 4.8 \times 10^{-6} \\ 3.9 \times 10^{-6} \\ 3.57 \times 10^{-6} \end{array}$	[136]	
Cassava starch 10 g	Waxy maize SNP 0% 2.5%	Glycerol 5 g	$1.62 imes 10^{-6} \ 0.97 imes 10^{-6}$	[131]	

Table 6. Cont.

SNP: starch nanoparticle.

5.3. Thermal Properties

Analysis of the glass transition temperature can be carried out by using DSC (differential scanning calorimetry) [19], DMA (dynamic mechanical analysis) [85], or TGA (thermogravimetry analysis) [95]. The parameters tested include glass transition temperature (T_g), onset temperature (T_o), melting point (T_m), and enthalpy change (Δ H) [95]. The mechanism of starch nanoparticles as a reinforcing material in increasing thermal stability involves the interaction between the reinforcing material and matrix, forming a barricade that can inhibit the transfer of heat and energy [141].

According to Hakke et al. [95], there is an increase in Δ H along with the addition of the reinforcing material used. The increasing Δ H is related to starch, with nanoparticle size having a wider active site to interact and bind to the packaging matrix, so it takes more energy to break the polymer structure. This theory is in line with another study on bioplastic with a waterborne polyurethane (WPU) matrix and a pea starch nanoparticle reinforcing material [133]. The enthalpy change in bioplastic with 0% reinforcing material is 2.34 J/g, which increases to 12.5 J/g with a 30% concentration of reinforcing material. However, these

results differ from the study by Mukurumbira et al. [85], where along with the addition of reinforcing material concentration, there was a decrease in Δ H. Bioplastic with matrix potato starch, 10% amadumbe starch nanoparticle reinforcing material, and glycerol plasticizer had a Δ H of 0.91 J/g, while in the sample without reinforcing material, the observed Δ H was 14.32 J/g. This could be related to the effect of starch nanoparticles on hindering the lateral arrangements of starch chains and the crystallization of starch films [85]. The thermal properties of bioplastics with various compositions of DSC measurements are shown in Table 7.

Bioplastic Composition							
Matrix	Reinforcing Material	Plasticizer	Τ _g (°C)	T _m (°C)	Т _о (°С)	ΔH (J/g)	Ref.
Potato starch	Amadumbe SNP 0% 2.5% 5% 10%	Glycerol 30%	64 72 94 94	78.19 88.59 107.31 105.52	78.19 88.59 107.31 105.52	14.32 16.69 2.39 0.91	[85]
Amadumbe starch	Amadumbe SNP 0% 2.5% 5% 10%	Glycerol 30%	60 70 86 92	66.03 72.49 73.07 96.24	66.03660324.9272.4972.4920.6873.0773.0715.6396.2496.2415.27		[00]
Corn starch 7.5 g	Taro SNP 0% 0.5% 2% 5% 10% 15%	Glycerol 3 g	NR	210.21 219.47 223.19 218.1 222.34 209.91	171.75 187.59 187.43 184.08 187.28 180.3	45.49 51.9 50.84 50.03 55.34 36.95	[109]
Pea starch 7.5 g	Potato SNP 0% 3% 6% 9% 12%	Glycerol 3 g	NR	225.81 226.91 227.2 231.98 235.81	192.97 195.01 196.43 199.58 200.08	42.75 24.72 22.24 32.51 34.32	[107]
Pea starch 5 g	Waxy maize SNP 0 1% 3% 5% 7% 9%	Glycerol 3%	NR	188.51 190.81 189.56 193.92 189.66 190.1	186.61 186.26 186.79 187.35 186.61 187.54	23.51 24.34 24.75 26.76 22.31 22.17	[135]
Waxy maize starch	Waxy maize SNP 0% 5% 10% 15%	Sorbitol 25%	40.1 46.3 52.3 58.8	150.1 152.7 160.4 169.7	NR	99.8 122.4 150.7 165.2	[139]

Table 7. Thermal properties of bioplastics with various compositions.

NR: not reported; SNP: starch nanoparticle.

5.4. Biodegradability

The biodegradability test was carried out to determine the time required for bioplastic packaging to decompose in the soil. Biodegradability causes a decrease in molecular weight, due to the activity of microorganisms, such as bacteria, microalgae, and fungi, resulting in molecular reduction [19]. This test can be performed by placing the film sample in a

container filled with soil, then observing the decrease in the weight of the film sample along with the length of the test [142]. During the degradation process, relative humidity plays a role in determining the biodegradation rate. Higher relative humidity can increase the growth of microorganisms, causing a higher rate of degradation [106].

The use of starch nanoparticles as a reinforcing material is effective in increasing the biodegradability of bioplastic packaging. A previous study has reported that within 1 week, bioplastic with a starch mung bean matrix and glycerol plasticizer experienced a weight loss of 28.67%. When adding 1% mung bean starch nanoparticle reinforcing material, in the same period, there was a decrease in packaging weight of 83.46%, and when 2–10% reinforcing material was added, the packaging was 100% degraded [143]. The use of corn starch nanoparticle reinforcing material also increases the biodegradability of PCL packaging. With the use of 10% reinforcing material, the observed weight loss reached 17.6 mg/cm^2 , whereas without reinforcing material, the observed weight loss was 7 mg/cm^2 . Then, the observed weight loss was more than 2 times [19]. An increase in biodegradability is due to the use of starch nanoparticles causing a decrease in the molecular mass of the packaging polymer; hence, the degradation process by microorganisms takes place more quickly [19]. According to González Seligra et al. [106], the use of starch nanoparticles causes an increase in the film's moisture content, thereby creating a more suitable condition for the growth of microorganisms. This condition increases the chance of microorganism attack. During the degradation process, relative humidity plays a role in determining the biodegradation rate. Higher relative humidity can increase the growth of microorganisms, causing a higher rate of degradation [106]. The biodegradation rate of starch-based bioplastic depends on the hydrophilicity of the matrices. It is directly related to the water absorption; the higher the water absorption, the higher biodegradation [144,145]. The biodegradability of bioplastics with various compositions is shown in Table 8.

Bioplastic Composition					
Matrix	Reinforcing Material	Plasticizer	Duration	Weight Loss	Ref.
Cassava starch (4)	Cassava SNP (0) (0.5) (5) (10)	Glycerol (2.1)	17 weeks	82.8% 82.4% 82.5% 84.7%	[19]
Polycaprolactone	Corn SNP 0 2.25 5 10	-	4 days	7 mg/cm ² 10 mg/cm ² 15.7 mg/cm ² 17.6 mg/cm ²	[132]
Pea starch	Pea SNP 0% 0.5% 1% 2% 5% 10%	Glycerol 50%	1 week	28.67% 49.25% 83.46% 100% 100%	[143]

Table 8. Biodegradability of bioplastics with various compositions.

SNP: starch nanoparticle.

6. Opportunities and Challenges

Improving the properties of bioplastic polymers is a primary challenge of achieving sustainability in the food and packaging industry [146–148]. Starch nanoparticles can be utilized to make other kinds of packaging, including edible packaging, active packaging, and smart packaging, in addition to being a reinforcing material in bioplastic packaging.

The usage of starch nanoparticles in edible packaging is safe because they are nontoxic [103]. The use of starch nanoparticles in active packaging can maintain the stability of the bioactive compounds contained in the packaging because these compounds are volatile compounds that are sensitive to certain conditions [136]. Fonseca et al. [149] conducted a study related to the stability of the carvacrol compound mixed with potato starch nanofiber. They found that potato starch nanofibercan be a vehicle for carvacrol release in active packaging.

The use of starch nanoparticles as a reinforcing material as well as in the packaging field in general still finds many obstacles in its commercialization business. This is because production costs have not been effective. After all, the number of adaptations of this technology is still very low. On the other hand, reinforcing materials from inorganic materials have been widely applied, so that the production costs are cheaper and can produce bioplastic packaging with good characteristics. This causes the price of bioplastic packaging with reinforcing materials from starch nanoparticles to be expensive, and the option of using reinforcing materials from inorganic materials is preferred [16].

7. Conclusions

Research related to bioplastics as an alternative to conventional plastics is increasingly being carried out. This is based on the environmentally friendly nature of bioplastics. However, bioplastics still have limited characteristics, such as low mechanical strength and high water vapor permeability; hence, reinforcing the material's role becomes important. The use of starch nanoparticle as a reinforcing material in bioplastic decreases the elongation at break and water vapor permeability, and increases tensile strength and biodegradability. In general, starch nanoparticles also increase the thermal stability of bioplastics. The concentration of reinforcing material that exceeds the maximum threshold has an impact on increasing water vapor permeability and decreasing the mechanical and thermal characteristics of bioplastic packaging because starch nanoparticles at excessive concentrations tend to form aggregates.

8. Future Research

Starch nanoparticles have a great opportunity to be developed in the packaging field, mainly because of environmental interest. Although starch nanoparticles have many advantages as reinforcing materials, the utilization of starch nanoparticles on an industrial scale is still limited because adaptation to the use of starch nanoparticles as reinforcing materials in packaging is still low, causing production costs to be high and ineffective. Hence, continuous research about nano-reinforced bioplastic is needed.

In bioplastic processing, the dispersion and homogeneity of mixing bioplastic with starch nanoparticles as a reinforcing material are also interesting to study to produce high-quality bioplastic. The modification of starch nanoparticles can also be a promising option to make better bioplastic characteristics. There have been several studies on starch nanoparticle modification, but the number is still very limited, and thus further research needs to be developed.

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References

- 1. Vasseghian, Y.; Dragoi, E.-N.; Almomani, F.; Le, V.T. Graphene Derivatives in Bioplastic: A Comprehensive Review of Properties and Future Perspectives. *Chemosphere* **2022**, *286*, 131892. [CrossRef] [PubMed]
- Almomani, F.A.; Shawaqfah, M.; Bhosale, R.R.; Kumar, A. Removal of Emerging Pharmaceuticals from Wastewater by Ozone-Based Advanced Oxidation Processes. *Environ. Prog. Sustain. Energy* 2016, 35, 982–995. [CrossRef]
- Jaderi, F.; Ibrahim, Z.Z.; Zahiri, M.R. Criticality Analysis of Petrochemical Assets Using Risk Based Maintenance and the Fuzzy Inference System. *Process Saf. Environ. Prot.* 2019, 121, 312–325. [CrossRef]
- Thunman, H.; Berdugo Vilches, T.; Seemann, M.; Maric, J.; Vela, I.C.; Pissot, S.; Nguyen, H.N.T. Circular Use of Plastics-Transformation of Existing Petrochemical Clusters into Thermochemical Recycling Plants with 100% Plastics Recovery. *Sustain. Mater. Technol.* 2019, 22, e00124. [CrossRef]
- da Silva, T.R.; de Azevedo, A.R.; Cecchin, D.; Marvila, M.T.; Amran, M.; Fediuk, R.; Vatin, N.; Karelina, M.; Klyuev, S.; Szelag, M. Application of Plastic Wastes in Construction Materials: A Review Using the Concept of Life-Cycle Assessment in the Context of Recent Research for Future Perspectives. *Materials* 2021, 14, 3549. [CrossRef] [PubMed]
- 6. Chen, Y.J. Bioplastics and Their Role in Achieving Global Sustainability. J. Chem. Pharm. Res. 2014, 6, 226–231.
- Karimi-Maleh, H.; Kumar, B.G.; Rajendran, S.; Qin, J.; Vadivel, S.; Durgalakshmi, D.; Gracia, F.; Soto-Moscoso, M.; Orooji, Y.; Karimi, F. Tuning of Metal Oxides Photocatalytic Performance Using Ag Nanoparticles Integration. *J. Mol. Liq.* 2020, 314, 113588. [CrossRef]
- 8. Wu, F.; Misra, M.; Mohanty, A.K. Tailoring the Toughness of Sustainable Polymer Blends from Biodegradable Plastics Via Morphology Transition Observed by Atomic Force Microscopy. *Polym. Degrad. Stab.* **2020**, *173*, 109066. [CrossRef]
- 9. Friedrich, D.; Luible, A. Supporting the Development Process for Building Products by the Use of Research Portfolio Analysis: A Case Study for Wood Plastics Composite Materials. *Case Stud. Constr. Mater.* **2016**, *4*, 49–54. [CrossRef]
- 10. Ansink, E.; Wijk, L.; Zuidmeer, F. No Clue About Bioplastics. Ecol. Econ. 2022, 191, 107245. [CrossRef]
- 11. Atiwesh, G.; Mikhael, A.; Parrish, C.C.; Banoub, J.; Le, T.-A.T. Environmental Impact of Bioplastic Use: A Review. *Heliyon* 2021, 7, e07918. [CrossRef]
- García-Depraect, O.; Bordel, S.; Lebrero, R.; Santos-Beneit, F.; Börner, R.A.; Börner, T.; Muñoz, R. Inspired by Nature: Microbial Production, Degradation and Valorization of Biodegradable Bioplastics for Life-Cycle-Engineered Products. *Biotechnol. Adv.* 2021, 53, 107772. [CrossRef]
- 13. Gadhave, R.; Das, A.; Mahanwar, P.; Gadekar, P. Starch Based Bio-Plastics: The Future of Sustainable Packaging. *Open J. Polym. Chem.* **2018**, *8*, 21–33. [CrossRef]
- 14. Meereboer, K.; Misra, M.; Mohanty, A. Review of Recent Advances in the Biodegradability of Polyhydroxyalkanoate (Pha) Bioplastics and Their Composites. *Green Chem.* **2020**, *22*, 5519–5558. [CrossRef]
- 15. Lim, C.; Yusoff, S.; Ng, C.G.; Lim, P.E.; Ching, Y.C. Bioplastic Made from Seaweed Polysaccharides with Green Production Methods. *J. Environ. Chem. Eng.* **2021**, *9*, 105895. [CrossRef]
- Abe, M.M.; Martins, J.R.; Sanvezzo, P.B.; Macedo, J.V.; Branciforti, M.C.; Halley, P.; Botaro, V.R.; Brienzo, M. Advantages and Disadvantages of Bioplastics Production from Starch and Lignocellulosic Components. *Polymers* 2021, *13*, 2484. [CrossRef] [PubMed]
- 17. Tian, H.; Xu, G. Processing and Characterization of Glycerol-Plasticized Soy Protein Plastics Reinforced with Citric Acid-Modified Starch Nanoparticles. *J. Polym. Environ.* **2011**, *19*, 582–588. [CrossRef]
- 18. Ramadoss, P.; Basha, K.; Kumari, S. Nanostarch Reinforced with Chitosan/Poly (Vinyl Pyrrolidone) Blend for in Vitro Wound Healing Application. *Polym.-Plast. Technol. Eng.* **2017**, *57*, 1400–1410.
- Costa, É.K.D.C.; de Souza, C.O.; da Silva, J.B.A.; Druzian, J.I. Hydrolysis of Part of Cassava Starch into Nanocrystals Leads to Increased Reinforcement of Nanocomposite Films. J. Appl. Polym. Sci. 2017, 134, 45311. [CrossRef]
- 20. He, W.; Wei, C. A Critical Review on Structural Properties and Formation Mechanism of Heterogeneous Starch Granules in Cereal Endosperm Lacking Starch Branching Enzyme. *Food Hydrocoll.* **2020**, *100*, 105434. [CrossRef]
- 21. Li, H.; Gilbert, R.G. Starch Molecular Structure: The Basis for an Improved Understanding of Cooked Rice Texture. *Carbohydr. Polym.* **2018**, *195*, 9–17. [CrossRef] [PubMed]
- 22. Apriyanto, A.; Compart, J.; Fettke, J. A Review of Starch, a Unique Biopolymer—Structure, Metabolism and in Planta Modifications. *Plant Sci.* **2022**, *318*, 111223. [CrossRef] [PubMed]
- 23. Vianna, T.C.; Marinho, C.O.; Marangoni, L., Jr.; 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] [PubMed]
- 24. Hosseini, S.N.; Pirsa, S.; Farzi, J. Biodegradable Nano Composite Film Based on Modified Starch-Albumin/Mgo; Antibacterial, Antioxidant and Structural Properties. *Polym. Test.* **2021**, *97*, 107182. [CrossRef]
- Zhang, K.; Zhao, D.; Guo, D.; Tong, X.; Zhang, Y.; Wang, L. Physicochemical and Digestive Properties of a- and B-Type Granules Isolated from Wheat Starch as Affected by Microwave-Ultrasound and Toughening Treatment. *Int. J. Biol. Macromol.* 2021, 183, 481–489. [CrossRef] [PubMed]
- 26. Zou, W.; Yu, L.; Liu, X.; Chen, L.; Zhang, X.; Qiao, D.; Zhang, R. Effects of Amylose/Amylopectin Ratio on Starch-Based Superabsorbent Polymers. *Carbohydr. Polym.* **2012**, *87*, 1583–1588. [CrossRef]

- Jha, P.; Dharmalingam, K.; Nishizu, T.; Katsuno, N.; Anandalakshmi, R. Effect of Amylose–Amylopectin Ratios on Physical, Mechanical, and Thermal Properties of Starch-Based Bionanocomposite Films Incorporated with Cmc and Nanoclay. *Starch Stärke* 2020, 72, 1900121. [CrossRef]
- Karakelle, B.; Kian-Pour, N.; Toker, O.S.; Palabiyik, I. Effect of Process Conditions and Amylose/Amylopectin Ratio on the Pasting Behavior of Maize Starch: A Modeling Approach. J. Cereal Sci. 2020, 94, 102998. [CrossRef]
- Marta, H.; Cahyana, Y.; Bintang, S.; Soeherman, G.P.; Djali, M. Physicochemical and Pasting Properties of Corn Starch as Affected by Hydrothermal Modification by Various Methods. *Int. J. Food Prop.* 2022, 25, 792–812. [CrossRef]
- Marta, H.; Cahyana, Y.; Arifin, H.R.; Khairani, L. Comparing the Effect of Four Different Thermal Modifications on Physicochemical and Pasting Properties of Breadfruit (*Artocarpus altilis*) Starch. *Int. Food Res. J.* 2019, 26, 269–276.
- Marta, H.; Cahyana, Y.; Djali, M. Densely Packed-Matrices of Heat Moisture Treated-Starch Determine the Digestion Rate Constant as Revealed by Logarithm of Slope Plots. J. Food Sci. Technol. 2021, 58, 2237–2245. [CrossRef] [PubMed]
- 32. Cahyana, Y.; Rangkuti, A.; Siti Halimah, T.; Marta, H.; Yuliana, T. Application of Heat-Moisture-Treated Banana Flour as Composite Material in Hard Biscuit. *CYTA J. Food* **2020**, *18*, 599–605. [CrossRef]
- Ashfaq, A.; Khursheed, N.; Fatima, S.; Anjum, Z.; Younis, K. Application of Nanotechnology in Food Packaging: Pros and Cons. J. Agric. Food Res. 2022, 7, 100270. [CrossRef]
- Bel Haaj, S.; Thielemans, W.; Magnin, A.; Boufi, S. Starch Nanocrystals and Starch Nanoparticles from Waxy Maize as Nanoreinforcement: A Comparative Study. *Carbohydr. Polym.* 2016, 143, 310–317. [CrossRef]
- 35. Le Corre, D.; Angellier-Coussy, H. Preparation and Application of Starch Nanoparticles for Nanocomposites: A Review. *React. Funct. Polym.* **2014**, *85*, 97–120. [CrossRef]
- 36. Gong, B.; Liu, W.; Tan, H.; Yu, D.; Song, Z.; Lucia, L.A. Understanding Shape and Morphology of Unusual Tubular Starch Nanocrystals. *Carbohydr. Polym.* **2016**, *151*, 666–675. [CrossRef]
- Qiu, C.; Wang, C.; Gong, C.; McClements, D.J.; Jin, Z.; Wang, J. Advances in Research on Preparation, Characterization, Interaction with Proteins, Digestion and Delivery Systems of Starch-Based Nanoparticles. *Int. J. Biol. Macromol.* 2020, 152, 117–125. [CrossRef] [PubMed]
- 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]
- 39. Boufi, S.; Bel Haaj, S.; 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]
- Pérez-Masiá, R.; López-Nicolás, R.; Periago, M.J.; Ros, G.; Lagaron, J.M.; López-Rubio, A. Encapsulation of Folic Acid in Food Hydrocolloids through Nanospray Drying and Electrospraying for Nutraceutical Applications. *Food Chem.* 2015, 168, 124–133. [CrossRef]
- 41. Raigond, P.; Raigond, B.; Kochhar, T.; Sood, A.; Singh, B. Conversion of Potato Starch and Peel Waste to High Value Nanocrystals. *Potato Res.* **2018**, *61*, 341–351. [CrossRef]
- Chin, S.F.; Azman, A.; Pang, S.C. Size Controlled Synthesis of Starch Nanoparticles by a Microemulsion Method. *J. Nanomater.* 2014, 2014, 763736. [CrossRef]
- 43. Chin, S.F.; Pang, S.C.; Tay, S.H. Size Controlled Synthesis of Starch Nanoparticles by a Simple Nanoprecipitation Method. *Carbohydr. Polym.* **2011**, *86*, 1817–1819. [CrossRef]
- 44. Kong, L.; Ziegler, G.R. Fabrication of Pure Starch Fibers by Electrospinning. *Food Hydrocoll.* **2014**, *36*, 20–25. [CrossRef]
- Abid, N.; Khan, A.M.; Shujait, S.; Chaudhary, K.; Ikram, M.; Imran, M.; Haider, J.; Khan, M.; Khan, Q.; Maqbool, M. Synthesis of Nanomaterials Using Various Top-Down and Bottom-up Approaches, Influencing Factors, Advantages, and Disadvantages: A Review. Adv. Colloid Interface Sci. 2022, 300, 102597. [CrossRef] [PubMed]
- Lu, X.; Xiao, J.; Huang, Q. Pickering Emulsions Stabilized by Media-Milled Starch Particles. *Food Res. Int.* 2018, 105, 140–149. [CrossRef] [PubMed]
- Patel, C.M.; Chakraborty, M.; Murthy, Z.V.P. Fast and Scalable Preparation of Starch Nanoparticles by Stirred Media Milling. *Adv. Powder Technol.* 2016, 27, 1287–1294. [CrossRef]
- 48. Li, H.; Yan, S.; Ji, J.; Xu, M.; Mao, H.; Wen, Y.; Wang, J.; Sun, B. Insights into Maize Starch Degradation by High Pressure Homogenization Treatment from Molecular Structure Aspect. *Int. J. Biol. Macromol.* **2020**, *161*, 72–77. [CrossRef]
- 49. Apostolidis, E.; Mandala, I. Modification of Resistant Starch Nanoparticles Using High-Pressure Homogenization Treatment. *Food Hydrocoll.* **2020**, *103*, 105677. [CrossRef]
- 50. Ding, Y.; Kan, J. Optimization and Characterization of High Pressure Homogenization Produced Chemically Modified Starch Nanoparticles. *J. Food Sci. Technol.* **2017**, *54*, 4501–4509. [CrossRef]
- Chutia, H.; Mahanta, C.L. Properties of Starch Nanoparticle Obtained by Ultrasonication and High Pressure Homogenization for Developing Carotenoids-Enriched Powder and Pickering Nanoemulsion. *Innov. Food Sci. Emerg. Technol.* 2021, 74, 102822. [CrossRef]
- Noor, N.; Gani, A.; Jhan, F.; Ashraf Shah, M.; ul Ashraf, Z. Ferulic Acid Loaded Pickering Emulsions Stabilized by Resistant Starch Nanoparticles Using Ultrasonication: Characterization, in Vitro Release and Nutraceutical Potential. *Ultrason. Sonochem.* 2022, 84, 105967. [CrossRef] [PubMed]
- 53. Akhavan, A.; Ataeevarjovi, E. The Effect of Gamma Irradiation and Surfactants on the Size Distribution of Nanoparticles Based on Soluble Starch. *Radiat. Phys. Chem.* **2012**, *81*, 913–914. [CrossRef]

- 54. 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]
- Teodoro, A.P.; Mali, S.; Romero, N.; de Carvalho, G.M. Cassava Starch Films Containing Acetylated Starch Nanoparticles as Reinforcement: Physical and Mechanical Characterization. *Carbohydr. Polym.* 2015, 126, 9–16. [CrossRef] [PubMed]
- Chaudhary, P.; Fatima, F.; Kumar, A. Relevance of Nanomaterials in Food Packaging and Its Advanced Future Prospects. J. Inorg. Organomet. Polym. Mater. 2020, 30, 5180–5192. [CrossRef]
- 57. Song, D.; Thio, Y.S.; Deng, Y. Starch Nanoparticle Formation Via Reactive Extrusion and Related Mechanism Study. *Carbohydr. Polym.* **2011**, *85*, 208–214. [CrossRef]
- 58. Da Silva, N.M.C.; Correia, P.R.C.; Druzian, J.I.; Fakhouri, F.M.; Fialho, R.L.L.; de Albuquerque, E.C.M.C. Pbat/Tps Composite Films Reinforced with Starch Nanoparticles Produced by Ultrasound. *Int. J. Polym. Sci.* 2017, 2017, 4308261. [CrossRef]
- 59. Minakawa, A.F.K.; Faria-Tischer, P.C.S.; Mali, S. Simple Ultrasound Method to Obtain Starch Micro- and Nanoparticles from Cassava, Corn and Yam Starches. *Food Chem.* **2019**, *283*, 11–18. [CrossRef]
- Bel Haaj, S.; Magnin, A.; Pétrier, C.; Boufi, S. Starch Nanoparticles Formation Via High Power Ultrasonication. *Carbohydr. Polym.* 2013, 92, 1625–1632. [CrossRef]
- Ahmad, A.N.; Lim, S.A.; Navaranjan, N.; Hsu, Y.-I.; Uyama, H. Green Sago Starch Nanoparticles as Reinforcing Material for Green Composites. *Polymer* 2020, 202, 122646. [CrossRef]
- 62. Fu, Z.-Q.; Wang, L.-J.; Li, D.; Wei, Q.; Adhikari, B. Effects of High-Pressure Homogenization on the Properties of Starch-Plasticizer Dispersions and Their Films. *Carbohydr. Polym.* **2011**, *86*, 202–207. [CrossRef]
- 63. Kim, H.-Y.; Lee, J.H.; Kim, J.-Y.; Lim, W.-J.; Lim, S.-T. Characterization of Nanoparticles Prepared by Acid Hydrolysis of Various Starches. *Starch Stärke* 2012, 64, 367–373. [CrossRef]
- 64. Namazi, H.; Dadkhah, A. Convenient Method for Preparation of Hydrophobically Modified Starch Nanocrystals with Using Fatty Acids. *Carbohydr. Polym.* 2010, *79*, 731–737. [CrossRef]
- Sadeghi, R.; Daniella, Z.; Uzun, S.; Kokini, J. Effects of Starch Composition and Type of Non-Solvent on the Formation of Starch Nanoparticles and Improvement of Curcumin stability in Aqueous Media. J. Cereal Sci. 2017, 76, 122–130. [CrossRef]
- Wu, X.; Chang, Y.; Fu, Y.; Ren, L.; Tong, J.; Zhou, J. Effects of Non-Solvent and Starch Solution on Formation of Starch Nanoparticles by Nanoprecipitation. *Starch Stärke* 2016, *68*, 258–263. [CrossRef]
- 67. Hebeish, A.; El-Rafie, M.H.; El-Sheikh, M.A.; El-Naggar, M.E. Ultra-Fine Characteristics of Starch Nanoparticles Prepared Using Native Starch with and without Surfactant. *J. Inorg. Organomet. Polym. Mater.* **2014**, *24*, 515–524. [CrossRef]
- 68. Hao, Y.; Chen, Y.; Li, Q.; Gao, Q. Preparation of Starch Nanocrystals through Enzymatic Pretreatment from Waxy Potato Starch. *Carbohydr. Polym.* **2018**, *184*, 171–177. [CrossRef]
- 69. Lin, X.; Sun, S.; Wang, B.; Zheng, B.; Guo, Z. Structural and Physicochemical Properties of Lotus Seed Starch Nanoparticles Prepared Using Ultrasonic-Assisted Enzymatic Hydrolysis. *Ultrason. Sonochem.* **2020**, *68*, 105199. [CrossRef]
- Kim, J.-Y.; Park, D.-J.; Lim, S.-T. Fragmentation of Waxy Rice Starch Granules by Enzymatic Hydrolysis. *Cereal Chem.* 2008, 85, 182–187. [CrossRef]
- Saeng-on, J.; Aht-Ong, D. Production of Starch Nanocrystals from Agricultural Materials Using Mild Acid Hydrolysis Method: Optimization and Characterization. *Polym. Renew. Resour.* 2017, *8*, 91–116. [CrossRef]
- 72. Gonçalves, 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]
- 73. Kumari, S.; Yadav, B.S.; Yadav, R.B. Synthesis and Modification Approaches for Starch Nanoparticles for Their Emerging Food Industrial Applications: A Review. *Food Res. Int.* **2020**, *128*, 108765. [CrossRef] [PubMed]
- Rajisha, K.R.; Maria, H.J.; Pothan, L.A.; Ahmad, Z.; Thomas, S. Preparation and Characterization of Potato Starch Nanocrystal Reinforced Natural Rubber Nanocomposites. *Int. J. Biol. Macromol.* 2014, 67, 147–153. [CrossRef]
- Valodkar, M.; Thakore, S. Thermal and Mechanical Properties of Natural Rubber and Starch Nanobiocomposites. *Int. J. Polym.* Anal. Charact. 2010, 15, 387–395. [CrossRef]
- Campelo, P.H.; Sant'Ana, A.S.; Pedrosa Silva Clerici, M.T. Starch Nanoparticles: Production Methods, Structure, and Properties for Food Applications. *Cur. Opin. Food Sci.* 2020, 33, 136–140. [CrossRef]
- 77. Lin, N.; Huang, J.; Chang, P.R.; Anderson, D.P.; Yu, J. Preparation, Modification, and Application of Starch Nanocrystals in Nanomaterials: A Review. *J. Nanomater.* **2011**, 2011, 573687. [CrossRef]
- Wu, J.; Huang, Y.; Yao, R.; Deng, S.; Li, F.; Bian, X. Preparation and Characterization of Starch Nanoparticles from Potato Starch by Combined Solid-State Acid-Catalyzed Hydrolysis and Nanoprecipitation. *Starch Stärke* 2019, *71*, 1900095. [CrossRef]
- 79. Sun, Q.; Li, G.; Dai, L.; Ji, N.; Xiong, L. Green Preparation and Characterisation of Waxy Maize Starch Nanoparticles through Enzymolysis and Recrystallisation. *Food Chem.* **2014**, *162*, 223–228. [CrossRef]
- Dukare, A.S.; Arputharaj, A.; Bharimalla, A.K.; Saxena, S.; Vigneshwaran, N. Nanostarch Production by Enzymatic Hydrolysis of Cereal and Tuber Starches. *Carbohydr. Polym. Technol. Appl.* 2021, 2, 100121. [CrossRef]
- Hedayati, S.; Niakousari, M.; Mohsenpour, Z. Production of Tapioca Starch Nanoparticles by Nanoprecipitation-Sonication Treatment. *Int. J. Biol. Macromol.* 2020, 143, 136–142. [CrossRef] [PubMed]
- 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]

- 83. Torres, F.G.; Arroyo, J.; Tineo, C.; Troncoso, O. Tailoring the Properties of Native Andean Potato Starch Nanoparticles Using Acid and Alkaline Treatments. *Starch Stärke* 2019, *71*, 1800234. [CrossRef]
- Suriya, M.; Reddy, C.K.; Haripriya, S.; Harsha, N. Influence of Debranching and Retrogradation Time on Behavior Changes of *Amorphophallus paeoniifolius* Nanostarch. Int. J. Biol. Macromol. 2018, 120, 230–236. [CrossRef] [PubMed]
- Mukurumbira, A.R.; Mellem, J.J.; Amonsou, E.O. Effects of Amadumbe Starch Nanocrystals on the Physicochemical Properties of Starch Biocomposite Films. *Carbohydr. Polym.* 2017, 165, 142–148. [CrossRef]
- 86. 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]
- LeCorre, D.; Bras, J.; Dufresne, A. Influence of Botanic Origin and Amylose Content on the Morphology of Starch Nanocrystals. J. Nanopart. Res. 2011, 13, 7193–7208. [CrossRef]
- Zhou, L.; He, X.; Ji, N.; Dai, L.; Li, Y.; Yang, J.; Xiong, L.; Sun, Q. Preparation and Characterization of Waxy Maize Starch Nanoparticles Via Hydrochloric Acid Vapor Hydrolysis Combined with Ultrasonication Treatment. *Ultrason. Sonochem.* 2021, 80, 105836. [CrossRef]
- Wang, B.; Lin, X.; Zheng, Y.; Zeng, M.; Huang, M.; Guo, Z. Effect of Homogenization-Pressure-Assisted Enzymatic Hydrolysis on the Structural and Physicochemical Properties of Lotus-Seed Starch Nanoparticles. *Int. J. Biol. Macromol.* 2021, 167, 1579–1586. [CrossRef]
- Shi, A.; Li, D.; Wang, L.-J.; Li, B.-Z.; Adhikari, B. Preparation of Starch-Based Nanoparticles through High-Pressure Homogenization and Miniemulsion Cross-Linking: Influence of Various Process Parameters on Particle Size and Stability. *Carbohydr. Polym.* 2011, *83*, 1604–1610. [CrossRef]
- 91. Dong, H.; Zhang, Q.; Gao, J.; Chen, L.; Vasanthan, T. Preparation and Characterization of Nanoparticles from Cereal and Pulse Starches by Ultrasonic-Assisted Dissolution and Rapid Nanoprecipitation. *Food Hydrocoll.* **2022**, *122*, 107081. [CrossRef]
- Ding, Y.; Zheng, J.; Zhang, F.; Kan, J. Synthesis and Characterization of Retrograded Starch Nanoparticles through Homogenization and Miniemulsion Cross-Linking. *Carbohydr. Polym.* 2016, 151, 656–665. [CrossRef] [PubMed]
- Silva, A.P.M.; Oliveira, A.V.; Pontes, S.M.A.; Pereira, A.L.S.; Souza Filho, M.D.S.M.; Rosa, M.F.; Azeredo, H.M.C. Mango Kernel Starch Films as Affected by Starch Nanocrystals and Cellulose Nanocrystals. *Carbohydr. Polym.* 2019, 211, 209–216. [CrossRef] [PubMed]
- 94. Oliveira, A.V.; da Silva, A.P.M.; Barros, M.O.; Filho, M.D.S.M.S.; Rosa, M.F.; Azeredo, H.M.C. Nanocomposite Films from Mango Kernel or Corn Starch with Starch Nanocrystals. *Starch Stärke* 2018, *70*, 1800028. [CrossRef]
- Hakke, V.S.; Landge, V.K.; Sonawane, S.H.; Babu, G.U.B.; Ashokkumar, M.; Flores, E.M.M. The Physical, Mechanical, Thermal and Barrier Properties of Starch Nanoparticle (Snp)/Polyurethane (Pu) Nanocomposite Films Synthesised by an Ultrasound-Assisted Process. *Ultrason. Sonochem.* 2022, *88*, 106069. [CrossRef] [PubMed]
- Sanchez de la Concha, B.B.; Agama-Acevedo, E.; Nuñez-Santiago, M.C.; Bello-Perez, L.A.; Garcia, H.S.; Alvarez-Ramirez, J. Acid Hydrolysis of Waxy Starches with Different Granule Size for Nanocrystal Production. J. Cereal Sci. 2018, 79, 193–200. [CrossRef]
- 97. Jeong, O.; Shin, M. Preparation and Stability of Resistant Starch Nanoparticles, Using Acid Hydrolysis and Cross-Linking of Waxy Rice Starch. *Food Chem.* 2018, 256, 77–84. [CrossRef]
- Piyada, K.; Sridach, W.; Thawien, W. Mechanical, Thermal and Structural Properties of Rice Starch Films Reinforced with Rice Starch Nanocrystals. *Int. Food Res. J.* 2013, 20, 439–449.
- 99. Jiang, S.; Liu, C.; Han, Z.; Xiong, L.; Sun, Q. Evaluation of Rheological Behavior of Starch Nanocrystals by Acid Hydrolysis and Starch Nanoparticles by Self-Assembly: A Comparative Study. *Food Hydrocoll.* **2016**, *52*, 914–922. [CrossRef]
- Mohammad Amini, A.; Razavi, S.M.A. A Fast and Efficient Approach to Prepare Starch Nanocrystals from Normal Corn Starch. *Food Hydrocoll.* 2016, 57, 132–138. [CrossRef]
- Dai, L.; Li, C.; Zhang, J.; Cheng, F. Preparation and Characterization of Starch Nanocrystals Combining Ball Milling with Acid Hydrolysis. *Carbohydr. Polym.* 2018, 180, 122–127. [CrossRef] [PubMed]
- Chavan, P.; Sinhmar, A.; Nehra, M.; Thory, R.; Pathera, A.K.; Sundarraj, A.A.; Nain, V. Impact on Various Properties of Native Starch after Synthesis of Starch Nanoparticles: A Review. *Food Chem.* 2021, 364, 130416. [CrossRef] [PubMed]
- Hernández-Jaimes, C.; Bello-Pérez, L.A.; Vernon-Carter, E.J.; Alvarez-Ramirez, J. Plantain Starch Granules Morphology, Crystallinity, Structure Transition, and Size Evolution Upon Acid Hydrolysis. *Carbohydr. Polym.* 2013, 95, 207–213. [CrossRef] [PubMed]
- 104. Chang, R.; Ji, N.; Li, M.; Qiu, L.; Sun, C.; Bian, X.; Qiu, H.; Xiong, L.; Sun, Q. Green Preparation and Characterization of Starch Nanoparticles Using a Vacuum Cold Plasma Process Combined with Ultrasonication Treatment. *Ultrason. Sonochem.* 2019, 58, 104660. [CrossRef]
- Chang, Y.; Yan, X.; Wang, Q.; Ren, L.; Tong, J.; Zhou, J. High Efficiency and Low Cost Preparation of Size Controlled Starch Nanoparticles through Ultrasonic Treatment and Precipitation. *Food Chem.* 2017, 227, 369–375. [CrossRef]
- González Seligra, P.; Eloy Moura, L.; Famá, L.; Druzian, J.I.; Goyanes, S. Influence of Incorporation of Starch Nanoparticles in Pbat/Tps Composite Films. *Polym. Int.* 2016, 65, 938–945. [CrossRef]
- Jiang, S.; Liu, C.; Wang, X.; Xiong, L.; Sun, Q. Physicochemical Properties of Starch Nanocomposite Films Enhanced by Self-Assembled Potato Starch Nanoparticles. *LWT Food Sci. Technol.* 2016, 69, 251–257. [CrossRef]

- Marta, H.; Cahyana, Y.; Djali, M.; Arcot, J.; Tensiska, T. A Comparative Study on the Physicochemical and Pasting Properties of Starch and Flour from Different Banana (Musa Spp.) Cultivars Grown in Indonesia. *Int. J. Food Prop.* 2019, 22, 1562–1575. [CrossRef]
- Dai, L.; Qiu, C.; Xiong, L.; Sun, Q. Characterisation of Corn Starch-Based Films Reinforced with Taro Starch Nanoparticles. *Food Chem.* 2015, 174, 82–88. [CrossRef]
- 110. Shlush, E.; Davidovich-Pinhas, M. Bioplastics for Food Packaging. Trends Food Sci. Technol. 2022, 125, 66-80. [CrossRef]
- 111. Nguyen, H.T.H.; Qi, P.; Rostagno, M.; Feteha, A.; Miller, S.A. The Quest for High Glass Transition Temperature Bioplastics. J. Mater. Chem. A 2018, 6, 9298–9331. [CrossRef]
- 112. Naser, A.Z.; Deiab, I.; Darras, B.M. Poly(Lactic Acid) (Pla) and Polyhydroxyalkanoates (Phas), Green Alternatives to Petroleum-Based Plastics: A Review. *RSC Adv.* 2021, *11*, 17151–17196. [CrossRef]
- Van Roijen, E.C.; Miller, S.A. A Review of Bioplastics at End-of-Life: Linking Experimental Biodegradation Studies and Life Cycle Impact Assessments. *Resour. Conserv. Recycl.* 2022, 181, 106236. [CrossRef]
- 114. Andreasi Bassi, S.; Boldrin, A.; Frenna, G.; Astrup, T.F. An Environmental and Economic Assessment of Bioplastic from Urban Biowaste. The Example of Polyhydroxyalkanoate. *Bioresour. Technol.* **2021**, 327, 124813. [CrossRef]
- 115. 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]
- Chia, W.Y.; Ying Tang, D.Y.; Khoo, K.S.; Kay Lup, A.N.; Chew, K.W. Nature's Fight against Plastic Pollution: Algae for Plastic Biodegradation and Bioplastics Production. *Environ. Sci. Ecotechnol.* 2020, *4*, 100065. [CrossRef] [PubMed]
- 117. Ding, Z.; Kumar, V.; Sar, T.; Harirchi, S.; Dregulo, A.M.; Sirohi, R.; Sindhu, R.; Binod, P.; Liu, X.; Zhang, Z.; et al. Agro Waste as a Potential Carbon Feedstock for Poly-3-Hydroxy Alkanoates Production: Commercialization Potential and Technical Hurdles. *Bioresour. Technol.* 2022, 364, 128058. [CrossRef]
- Bátori, V.; Jabbari, M.; Åkesson, D.; Lennartsson, P.R.; Taherzadeh, M.J.; Zamani, A. Production of Pectin-Cellulose Biofilms: A New Approach for Citrus Waste Recycling. Int. J. Polym. Sci. 2017, 2017, 9732329. [CrossRef]
- 119. Giosafatto, C.; Al-Asmar, A.; D'Angelo, A.; Roviello, V.; Esposito, M.; Mariniello, L. Preparation and Characterization of Bioplastics from Grass Pea Flour Cast in the Presence of Microbial Transglutaminase. *Coatings* **2018**, *8*, 435. [CrossRef]
- Adorna, J.A.; Ventura, R.L.G.; Dang, V.D.; Doong, R.-A.; Ventura, J.-R.S. Biodegradable Polyhydroxybutyrate/Cellulose/Calcium Carbonate Bioplastic Composites Prepared by Heat-Assisted Solution Casting Method. J. Appl. Polym. Sci. 2022, 139, 51645. [CrossRef]
- Félix, M.; Lucio-Villegas, A.; Romero, A.; Guerrero, A. Development of Rice Protein Bio-Based Plastic Materials Processed by Injection Molding. *Ind. Crops Prod.* 2016, 79, 152–159. [CrossRef]
- Alonso-González, M.; Felix, M.; Romero, A. Influence of the Plasticizer on Rice Bran-Based Eco-Friendly Bioplastics Obtained by Injection Moulding. *Ind. Crops Prod.* 2022, 180, 114767. [CrossRef]
- 123. Srisuwan, Y.; Baimark, Y. Mechanical Properties and Heat Resistance of Stereocomplex Polylactide/Copolyester Blend Films Prepared by in Situ Melt Blending Followed with Compression Molding. *Heliyon* **2018**, *4*, e01082. [CrossRef]
- 124. Jiménez-Rosado, M.; Zarate-Ramírez, L.S.; Romero, A.; Bengoechea, C.; Partal, P.; Guerrero, A. Bioplastics Based on Wheat Gluten Processed by Extrusion. J. Clean. Prod. 2019, 239, 117994. [CrossRef]
- 125. Mathiot, C.; Ponge, P.; Gallard, B.; Sassi, J.-F.; Delrue, F.; Le Moigne, N. Microalgae Starch-Based Bioplastics: Screening of Ten Strains and Plasticization of Unfractionated Microalgae by Extrusion. *Carbohydr. Polym.* **2019**, 208, 142–151. [CrossRef] [PubMed]
- 126. Gug, J.; Soule, J.; Tan, B.; Sobkowicz, M.J. Effects of Chain-Extending Stabilizer on Bioplastic Poly(Lactic Acid)/Polyamide Blends Compatibilized by Reactive Extrusion. *Polym. Degrad. Stab.* **2018**, *153*, 118–129. [CrossRef]
- Gustafsson, J.; Landberg, M.; Bátori, V.; Åkesson, D.; Taherzadeh, M.J.; Zamani, A. Development of Bio-Based Films and 3d Objects from Apple Pomace. *Polymers* 2019, *11*, 289. [CrossRef] [PubMed]
- 128. Perez-Puyana, V.; Felix, M.; Romero, A.; Guerrero, A. Effect of the Injection Moulding Processing Conditions on the Development of Pea Protein-Based Bioplastics. J. Appl. Polym. Sci. 2016, 133, 43306. [CrossRef]
- Afiq, M.M.; Azura, A.R. Effect of Sago Starch Loadings on Soil Decomposition of Natural Rubber Latex (Nrl) Composite Films Mechanical Properties. *Int. Biodeterior. Biodegrad.* 2013, 85, 139–149. [CrossRef]
- 130. Jayathilaka, L.P.I.; Ariyadasa, T.U.; Egodage, S.M. Development of Biodegradable Natural Rubber Latex Composites by Employing Corn Derivative Bio-Fillers. *J. Appl. Polym. Sci.* 2020, 137, 49205. [CrossRef]
- García, N.L.; Ribba, L.; Dufresne, A.; Aranguren, M.I.; Goyanes, S. Physico-Mechanical Properties of Biodegradable Starch Nanocomposites. *Macromol. Mat. Eng.* 2009, 294, 169–177. [CrossRef]
- 132. Kong, J.; Yu, Y.; Pei, X.; Han, C.; Tan, Y.; Dong, L. Polycaprolactone Nanocomposite Reinforced by Bioresource Starch-Based Nanoparticles. *Int. J. Biol. Macromol.* **2017**, *102*, 1304–1311. [CrossRef]
- 133. Zou, J.; Zhang, F.; Huang, J.; Chang, P.R.; Su, Z.; Yu, J. Effects of Starch Nanocrystals on Structure and Properties of Waterborne Polyurethane-Based Composites. *Carbohydr. Polym.* **2011**, *85*, 824–831. [CrossRef]
- 134. Dai, L.; Zhang, J.; Cheng, F. Cross-Linked Starch-Based Edible Coating Reinforced by Starch Nanocrystals and Its Preservation Effect on Graded Huangguan Pears. *Food Chem.* **2020**, *311*, 125891. [CrossRef] [PubMed]
- Li, X.; Qiu, C.; Ji, N.; Sun, C.; Xiong, L.; Sun, Q. Mechanical, Barrier and Morphological Properties of Starch Nanocrystals-Reinforced Pea Starch Films. *Carbohydr. Polym.* 2015, 121, 155–162. [CrossRef] [PubMed]

- González, A.; Alvarez Igarzabal, C.I. Nanocrystal-Reinforced Soy Protein Films and Their Application as Active Packaging. Food Hydrocoll. 2015, 43, 777–784. [CrossRef]
- 137. Duan, B.; Sun, P.; Wang, X.; Yang, C. Preparation and Properties of Starch Nanocrystals/Carboxymethyl Chitosan Nanocomposite Films. *Starch Starke* 2011, *63*, 528–535. [CrossRef]
- Kristo, E.; Biliaderis, C.G. Physical Properties of Starch Nanocrystal-Reinforced Pullulan Films. Carbohydr. Polym. 2007, 68, 146–158. [CrossRef]
- 139. Viguié, J.; Molina-Boisseau, S.; Dufresne, A. Processing and Characterization of Waxy Maize Starch Films Plasticized by Sorbitol and Reinforced with Starch Nanocrystals. *Macromol. Biosci.* **2007**, *7*, 1206–1216. [CrossRef]
- 140. García, N.L.; Ribba, L.; Dufresne, A.; Aranguren, M.; Goyanes, S. Effect of Glycerol on the Morphology of Nanocomposites Made from Thermoplastic Starch and Starch Nanocrystals. *Carbohydr. Polym.* **2011**, *84*, 203–210. [CrossRef]
- 141. Basavegowda, N.; Baek, K.-H. Advances in Functional Biopolymer-Based Nanocomposites for Active Food Packaging Applications. *Polymers* **2021**, *13*, 4198. [CrossRef] [PubMed]
- 142. Priyadarshini, R.; Palanisami, T.; Pugazhendi, A.; Gnanamani, A.; Karthik, O. Plastic to Bioplastic (P2bp): A Green Technology for Circular Bioeconomy. *Front. Microbiol.* **2022**, *13*, 851045. [CrossRef] [PubMed]
- Roy, K.; Thory, R.; Sinhmar, A.; Pathera, A.K.; Nain, V. Development and Characterization of Nano Starch-Based Composite Films from Mung Bean (*Vigna radiata*). *Int. J. Biol. Macromol.* 2020, 144, 242–251. [CrossRef]
- Wadaugsorn, K.; Panrong, T.; Wongphan, P.; Harnkarnsujarit, N. Plasticized Hydroxypropyl Cassava Starch Blended Pbat for Improved Clarity Blown Films: Morphology and Properties. *Ind. Crops Prod.* 2022, 176, 114311. [CrossRef]
- Wongphan, P.; Khowthong, M.; Supatrawiporn, T.; Harnkarnsujarit, N. Novel Edible Starch Films Incorporating Papain for Meat Tenderization. *Food Packag. Shelf Life* 2022, 31, 100787. [CrossRef]
- 146. Srisa, A.; Promhuad, K.; San, H.; Laorenza, Y.; Wongphan, P.; Wadaugsorn, K.; Sodsai, J.; Kaewpetch, T.; Tansin, K.; Harnkarnsujarit, N. Antibacterial, Antifungal and Antiviral Polymeric Food Packaging in Post-COVID-19 Era. *Polymers* 2022, 14, 4042. [CrossRef] [PubMed]
- 147. Promhuad, K.; Srisa, A.; San, H.; Laorenza, Y.; Wongphan, P.; Sodsai, J.; Tansin, K.; Phromphen, P.; Chartvivatpornchai, N.; Ngoenchai, P.; et al. Applications of Hemp Polymers and Extracts in Food, Textile and Packaging: A Review. *Polymers* 2022, 14, 4274. [CrossRef]
- 148. San, H.; Laorenza, Y.; Behzadfar, E.; Sonchaeng, U.; Wadaugsorn, K.; Sodsai, J.; Kaewpetch, T.; Promhuad, K.; Srisa, A.; Wongphan, P.; et al. Functional Polymer and Packaging Technology for Bakery Products. *Polymers* **2022**, *14*, 3793. [CrossRef]
- Fonseca, L.M.; Cruxen, C.E.D.S.; Bruni, G.P.; Fiorentini, Â.M.; Zavareze, E.D.R.; Lim, L.-T.; Dias, A.R.G. Development of Antimicrobial and Antioxidant Electrospun Soluble Potato Starch Nanofibers Loaded with Carvacrol. *Int. J. Biol. Macromol.* 2019, 139, 1182–1190. [CrossRef]