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Starch Nanocrystal and its Food Packaging Applications

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Abstract

Food packaging is a crucial medium for protecting food from contamination, and spoilage by intrinsic and extrinsic factors. Nevertheless, for the past two decades, packaging materials have become environmental concern due to their disposal challenges. Starch is an eco-friendly packaging alternative, and it possesses outstanding degradability and reproducibility. The objective of this review is to examine the different methods used for the synthesis of nanostarch and expose their food packaging applications. Major sources of bibliometric information such as Web of Science, Scopus, PubMed, and Google Scholar were extensively searched with keywords such as starch, nano starch, starch nanocrystal, bio-composite film, acid hydrolysis, cassava starch, maize starch, edible film etc., to obtain a database of 272 papers. Thirty-nine publications met the criteria for review. The application of biopolymers such as starch, protein, and cellulose in the manufacturing of biodegradable films is an innovative approach. Starch is considered a promising biopolymer owing to its low cost, biodegradability, diversity, and availability. Currently, nanotechnology has received a lot of importance in the food packaging sector. Biodegradable nanocomposite packaging is an innovative technique to wrap food for enhanced shelf-life. Numerous food components are employed in the development of nanoparticles which includes proteins, starch, lipids, and polysaccharides. Nanostarch has certain unique properties such as being biocompatible, less expensive, biodegradable, sustainable, and eco-friendly nature. At present, nanostarch based packaging is prepared by mixing starch and non-starch polymers such as chitosan, cellulose, gelatin, whey protein etc. to increase

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mechanical property. Hence, the preparation of starch nanocrystals-based packaging material presents a substantial improvement in barrier properties, tensile strength, elastic modulus and food quality, and shelf life. The present review gives a comprehensive understanding of the synthesis and characterization of the starch nanocrystal, its food packaging application, sustainability, and regulatory aspects alongside new perspectives which is inadequate in the literature.

Introduction

Food is one of the basic human needs. Foods derived from plants and animals contain essential nutrients such as moisture, carbohydrates, proteins, fats, minerals, vitamins, and other non-nutrients.[1] Food items get spoiled due to biological, chemical, environmental or physical factors. Among them, the biological (caused by microorganisms) and environmental factors including temperature, moisture, oxygen, and light can cause several undesirable changes in the food that leads to either rejection or riskiness to consumers.[2] The major sustainable development goal of the United States is to eradicate hunger and to feed 10 billion global populations by 2050. Further, it create trade-offs between food security, sustainability, food safety, and food produced.[3] A reliable food supply with an emphasis on food deterioration, storage, and transport is necessary to accomplish the goal.[4] Food spoilage may alter the nutritional values, flavor, colour, texture, and palatability of the product.[1] Hence, foods need to be preserved from spoilage to maintain their quality for a prolonged period.

Food preservation refers to the process or method applied to control both internal and external factors which may cause deterioration of food. Therefore, food preservation plays an important role in extending the shelf life and retaining food quality and food safety.2 This is achieved by controlling enzymatic activity, certain chemical compounds in food, and spoilage microorganisms.[5]

Preservation is usually associated with various food processing steps to attain a desirable food quality and nutritional value. Food preservation methods include but are not limited to refrigeration, freezing, canning, drying and dehydration, packaging, smoking, application of food additives, modified or controlled atmospheric storage, and irradiation.[2] In spite of the scientific advances in preservation technologies, several food items still depend on conventional methods for storage such as dehydration, low temperature, osmosis, wood smoking, or organic chemicals.[6] Nevertheless, some novel food processing and preservation techniques are developed to enhance the shelf life of several foodstuffs. Emerging non-thermal food processing technologies includes cold plasma, ohmic heating, high pressure, pulsed electric field, and ultraviolet irradiation.[7]

Among the several food preservation techniques, packaging plays a crucial role in every stage of the food industry also in the preservation and storage of food products during the entire supply chain. Recently, food packaging has received great attention as it offers high-quality food with an extended shelf life to consumers. As a result, innovations were done in smart packaging which would possess active compounds, excellent barrier properties, and biodegradability to reduce environmental pollution.[8] Currently, the application of nanomaterials in food packaging is found to be a promising area to enhance the functionality of packaging material.[9]

Nanotechnology deals with the production, manipulation, and evaluation of materials at the nano size ranging between 1-100 nm. When the size of the particle is reduced to the nano level, it exhibits significantly different chemical properties than in its macrosize.[10] Numerous food components are used for the development of nanoparticles which include carbohydrates particularly starch, cellulose etc. protein, lipids, minerals, and surfactants.[11,12] These nanomaterials present an excellent advantage in terms of biodegradability and biocompatibility in food packaging applications.[13,14] The composition of the nanoparticles is altered by their physicochemical, protecting, releasing, and encapsulating capabilities.[14,15] To address this drawback, new methods including nanocapsules, nanoemulsions, nanospheres, nanofibers and nanoliposomes are developed to prepare food packaging material in the food industry.[16] Rice starch and potato starch nanocrystals prepared by acid hydrolysis (3.16M sulfuric acid) were used in the starch-based films. Application of starch nanocrystals in the films has reduced water vapor permeability, increased crystallinity, reduced the surface roughness, and fracture.[17] However, food packaging using nanomaterials remains the most under-exploited area of research in the field of food science and nanotechnology.[10] This review incorporated the literature on starch-based bio-nanocomposites, enabling the creation of new frameworks and perspectives on nanostarch packaging systems. Hence the present review prudently compiles information about the functions of packaging, sources of starch, methods for the synthesis of nanostarch, characterization of nanostarch, and regulatory aspects of nanomaterials in packaging.

Functions of Food Packaging

Food packaging is viewed as a marketing tool for food products in the industry, and it also aids in grabbing consumers' attention.[18,19] The main purpose of food packaging is to communicate information, containment, protection, ease of handling, and facilitation of handling (Figure 1). The protective function includes mechanical protection, barriers (against oxygen or water vapour), thermal, and sealing properties. The 'facilitate handling' function includes features such as unitization, apportionment, resealability, and emptying. Communication functions consist mostly of product and packaging information and instructions, as in how to properly store, open, and dispose of the package. Moreover, instructions for extending the shelf life of packaged food's by encouraging consumers to freeze leftovers may be included on the packaging.[14,20,21] Secondary functions of packaging include convenience, freshness indication, damage indication, and traceability. Traditional packaging such as gunny bags, glass jars, courier bags, cardboard, bubble envelopes, cartons, etc. are typically applied for a finished product.[22]

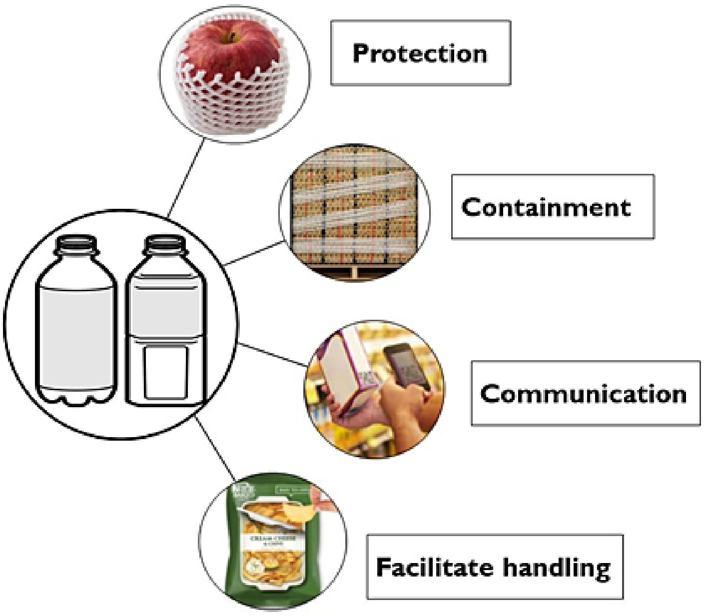

Fig. 1: Functions of food packaging

Different Types of Packaging Include

1. Primary packaging
2. Secondary packaging
3. Tertiary packaging

Primary Packaging

It is the packaging material which is in direct contact with the food items. It encloses, holds and protects the food from the external environment. It is the smallest system of distribution. The form, dimensions, and consistency of the product determine the main priorities for primary packaging. Depending on the product, transit, and storage conditions, primary packaging can serve diverse applications and functions. The most evident and crucial function is to protect and preserve the product from external damage, contamination, spoilage, and chemical imbalances. Moreover, primary packaging keeps a product in storage, often for longer periods.
Example: Chips packet

Secondary Packaging

It is the material that lies exterior to primary packaging and helps to group the primary packages together and further protect and label the food product. The two primary purposes of secondary packaging are branding and display and logistics. Secondary packaging is essential in marketing the product. When it comes to displaying packing, this is extremely important. It makes handling, transporting, and storing several products easier. Secondary packaging is intended to protect not only the product but also the primary packaging, which often is the packaging most visible to the consumer in retail displays
Example: Paperboard cartons of cornflakes, shrink wrapped bundles etc.,

Tertiary Packaging

Tertiary packaging material usually holds the secondary packages which facilitate handling bulk packaging, transportation, distribution, or storage. It not only protects the product but also the primary and secondary packaging. It serves three different functions

Protection

The primary purpose of tertiary packaging is to safeguard the product while it is being transported. Given the nature of the road and rail infrastructure, tertiary packaging should be made to withstand natural disasters like humidity, extreme heat, and severe weather, as well as unintentional shocks, impacts, and accidents of any kind.

Versatility

While designing tertiary packaging, keep in mind that there may be several stages in transit before the product reaches its final location. Multiple off-loading, re-packaging, re-loading, and even product storage are included in this.

Customized Solutions

Tertiary packaging should be as unique as the product itself and have the same size, shape, and consistency as the product. The emphasis in this case is on the packaging that is as compact, durable, and that takes up as little space as possible.
Examples: Brown cardboard boxes, wood pallets etc.

The major functions of packaging[14,21,22] (illustrated in Figure 2) are listed below.

1. The basic function of food packaging is to protect the food from external factors such as the environment which include humidity, sunlight, water vapour, oxygen, heat, or physical damage during transportation, distribution, and storage.
2. It also aids in preserving the food in its original state and provides information about the nutritional and ingredients information.
3. Indication of tampering, freshness, shelf life, and traceability is other functions of packaging.
4. It supports marketing of the product by providing the identity and ensures that it adapt to the specifications, laws, and regulation of the governing body.
5. It enhances the shelf life of the food products
6. It offers the consumer convenience in handling the product

Environmental Impact of Food Packaging

Food packaging is made up of several materials which may include plastic, laminates, coated sheets, films, paper, metals etc. These materials decompose at different rates while some of them undergo minimum degradation. Some materials like plastic when discarded affect the environment and seriously damage the ecosystem as they are made up of polyethylene, polystyrene, and polyvinyl chloride. Hence, they are considered a hazard to the environment.[14,23] Packaging material such as wood and paper are obtained from forest resources and the production of these material releases toxic gasses into the atmosphere. These toxic gases are not only harmful to humans but also to other animals. Non-degradable packaging systems when disposed of remain for a prolonged period abolish soil components which directly affect the agriculture productivity. Further, these consequences will result in food insecurity. Packaging waste as dumped on land would become a threat to animal life while disposed within the ocean will demine aquatic life.[23,24]

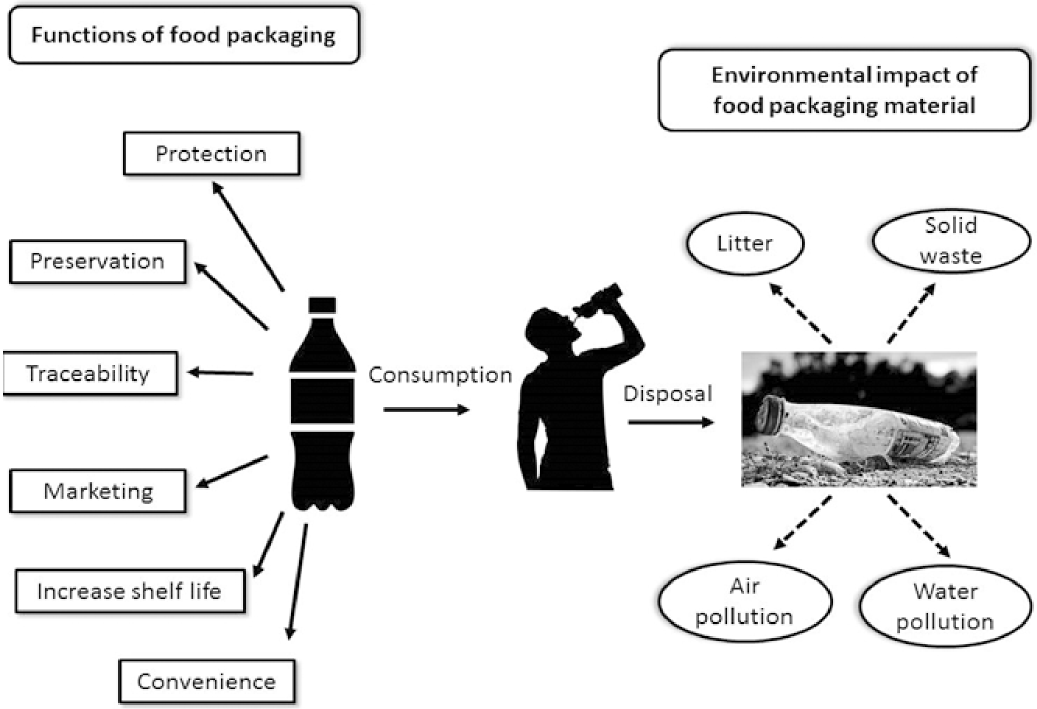

Fig. 2: An illustration showing the functions of food packaging and their environmental impact

Litter

Litter is usually associated with packaging material and is a part of total waste yet is a matter of concern because of its hazardous effect on human, animal, and marine life. The constituents of packaging substances including plastic bottles, glass, paper cups, and plastic wrappings are the major components of litter. Litter of plastic origin is the chief concern for an aquatic environment. It generates from land and sea sources, and the debris such as fishing gear including nylon buoys, lines, and nets; synthetic ropes, packaging bands, starps, and general litter, such as plastic sheeting, bags, and bootless.[25,26] Few studies have reported a positive correlation between plastic debris and the bioaccumulation of hazardous chemicals, a presentation that the concentrations of polychlorinated biphenyls (PCBs) and trace metals in seabirds and higher brominated polybrominated diphenyl ethers (PBDEs) were positively related with plastic debris.[27]

Water Pollution

Water pollution is originated by discharging the sludge obtained during the manufacturing of packaging substances. The major cause of water pollution is paper production as its waste effluent releases biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids, and volatile suspended solids (VSS). Moreover, the manufacturing of other packaging materials which include dye, coatings, and adhesives causes hydrocarbon pollution. While discharging thermoelectric cooling water leads to thermal pollution and accidental emissions particularly fire accidents during production or processing activities are also a matter of concern.[26,28] Landfill leachates cause water pollution, which are the product remnants of the packaging materials. Historical packaging can also be the source of organic plasticizers for PVC, or lead and cadmium from pigments.[29]

Air Pollution

Food packaging manufacturing is also one of the factors for air pollution. The components released during fire accidents at the workplace or incineration activities for waste disposal which include chlorofluorocarbons, vinyl chloride, and hexane pollute the environment. Dumping packaging waste at landfill sites undergoes decomposition and releases CO_2 and methane. Carbon dioxide is also released during the production of glass and steel for packaging applications. In addition, emissions corresponding to electricity generation and transportation are also part of environmental pollution.[26,28] In addition, packaging-related sources of air pollution from electricity generation (CO_2,SO_2, and NOx emissions) and logistics-related emissions including CO_2,SO_2, NOx, hydrocarbons, and dust. The need of accounting for emissions associated with transportation is rising, especially when reuse or recovery is being considered.[29]

Solid Waste

Solid waste is generated during the extraction and processing of raw material for packaging material which will be directed to landfill sites. Solid waste is categorized as pre-consumer and post-consumer solid waste. In general, pre-consumer waste produced from the industry is recycled while non-recyclable waste is discarded. Whereas, post-consumer solid waste needs more attention to recycle the materials however, not all collected materials are recycled as few products made from recycled waste will sooner be waste again. Hence, incineration of post-consumer packaging waste can reduce a volume reduction of about 20 to 40 %.[26,28]

Synthetic food packaging materials of petroleum origin and their constitutent materials are non-degradable and have become a severe environmental concerns. Synthetic materials such as low-density polyethylene (LDPE), polyester, polyvinylchloride, and high-density polyethylene (HDPE) materials are most commonly used in the packaging industry.[30,31] Hence these materials are restricted for packaging applications and researchers are working on an eco-friendly alternative natural polymer. Starch is found to be one of the most promising natural polymers for developing sustainable material due to its biodegradability, renewability, and low cost.[32]

Starch Sources, Production Statistics, and Nanostarch

Starch is a most abundant natural biological macromolecule which has great industrial applications. It is a renewable and biodegradable storage polysaccharide in plants. The chemical formula of starch is $(C_6H_{10}O_5)_n$. Starch is composed of two polymeric components named amylose and amylopectins. Amylose is a low molecular weight and long-chain linear polysaccharide of glucose linked by α-1,4 glycosidic bonds while amylopectin is a short and highly branched polymer linked by both α-1,4 glycosidic and α-1,6 glycosidic bonds.[33,34] Amylose (20-30%) and amylopectin (70-80%) content of the starch varies according to the source from which they are extracted.[35] The amylose and amylopectin molecules in the starch are arranged as crystalline clusters of double helical structure, forming stacks of alternative crystalline and amorphous lamella. The size (0.5- 175μm), shape and structural arrangement of the starch granules usually depend on the plant genotype, cultural practices, and environmental interactions.[36] The major source of starch includes corn, tapioca, potato, wheat, and sweet potato for industrial applications, whereas rice, sorghum, barley etc. are used as a minor source of starch around the globe. In addition, starch is also commercially isolated from rice, arrowroots, mung bean, and sago.[37] Corn starch is in high demand because of its textural (Figure 3) properties, especially as a thickening agent in industries such as dairy and beverages.

According to the global industrial starch market report (2020-2028), the market value of starch for the year 2020 was USD 97.85 billion and is expected to be increased by 7% between 2020 and 2028. Global production of starch has been estimated between 88.1 and 97.7 million tons in 2020.

Corn starch accounts for 75% of this amount, followed by cassava (14%), wheat (7%), and potato starches (4%).38.39 These statistics indicate that there is a great interest in exploring new starch sources for industrial applications.

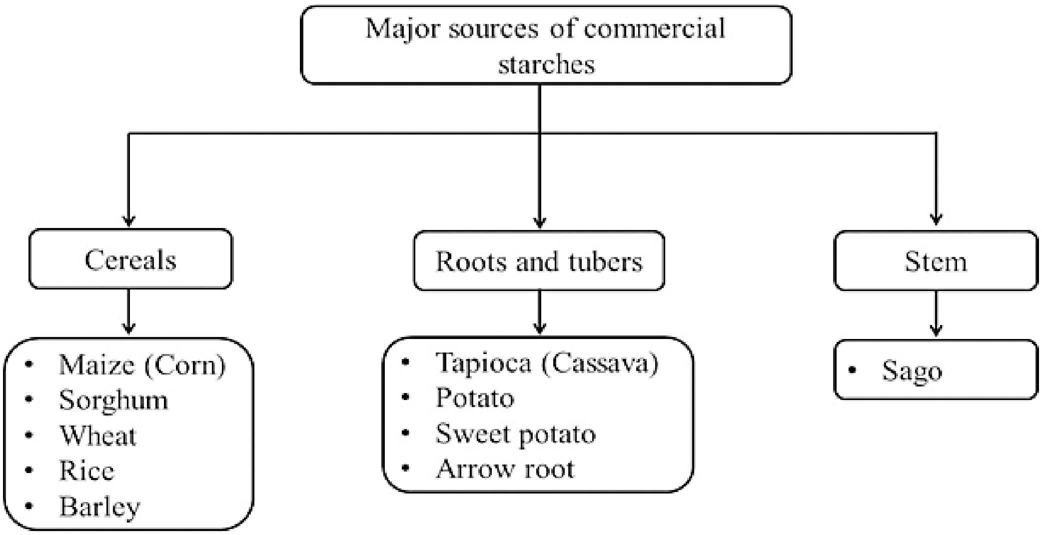

Fig. 3: Different sources of commercial starches

It is among the important polymers that find a wide application in food industries as a thickening agent, bulking agent, preservative, stabilizer, fat replacer, and quality improver in bakery products, extruded products, dairy products, confectioneries, soups, noodles, mayonnaises etc.[40] The diverse applications of starch are influenced by their physicochemical, functional, thermal properties. However, starch in its native form has limited applications and hence they are subjected to modifications for versatile use.[41] One such industrial application which received profound interest is starch-based biodegradable food packaging which reduces environmental pollution.[42]

Starch is an ideal material to produce nanoparticles or nanocrystals as it is a biodegradable natural polymer. In recent times, starch-based nanomaterials gained focus because of their unique properties, and biodegradable nature.[43] Starch-based nanomaterials are produced by various techniques including physical, chemicals, and enzymatic methods, and would be employed as a sensor for quality indication in food products, and reinforcement biodegradable or nonbiodegradable polymeric matrix.[44] Starch-based nanosystems are classified into two types based on their crystallinity as starch nanocrystals and starch nanoparticles. Starch nanocrystals are produced from disorganized semi-crystalline starch granules when heated below their gelatinization temperature. Starch nanocrystals are produced commonly by acid hydrolysis and have wide application in food as nanofiller for reinforcement of nanocomposites [45,46] emulsion stabilizers.[47,48]

While starch nanoparticles are nanosized amorphous starch granules with crystallinity of less than 10%. They are used as a carrier systems for drug delivery. Starch nanoparticles are prepared by using several methods such as ultrasonication, nanoprecipitation, high-pressure homogenization etc.[14,49] Starch-based nanosystem offers numerous benefits including lower viscosity, greater surface area, and better delivery efficiency of active compounds.[50,51] Starch-based nanosystems have been developed from various botanical sources such as potato starch,[52,53] cassava starch,[54] banana starch,[55] corn starch,[56] wheat starch,[57] chestnut starch,[58] lotus seed starch.[59] Application of nanosized (1-100 nm) organic or inorganic particles to starch-based thermoplastics offers a contemporary and extraordinary packaging technology, which is known as nano-inforced packaging material.[31] This type of packaging material provides good flexibility, biodegradability, and less molecular mass. In addition, its tensile strength is similar to low-density polyethylene (LDPE). Moreover, these types of nano-packaging systems are demonstrated to act as a barrier against moisture, oxygen, and microorganisms.[31,60]

Techniques for the Synthesis of Starch Nanocrystals

Starch nanocrystals can be developed by different methods including acid hydrolysis, enzymatic hydrolysis, ultrasound treatment, and a combination of these methods.[61,62,63] (Table 1). Several factors affect the yield, morphology, and properties of starch nanocrystals and further their industrial applications. Based on the literature, the yield of the starch nanocrystals is mainly influenced by the amylose content and the hydrolysis conditions whereas the size of the nanocrystal depends on the botanical source of the starch granules, degree of crystallinity, and their amylose levels.[61,64,65]

Acid Hydrolysis

Acid hydrolysis is the most predominant method used for the synthesis of starch nanocrystals. In general, starches are subjected to a two-stage hydrolysis reaction: the first stage is characterized by rapid hydrolysis where the amorphous regions of starch granules are attacked. While the second stage involves a slow hydrolysis reaction in which the crystalline portions get cleaved.[66,67] Few studies reported three stages of reactions involving rapid, slow, and very slow hydrolysis.[68,69]

Starch nanocrystals synthesized by this method exhibit a platelet-like shape with a high degree of crystallinity. During the synthesis process, starch is mixed with a dilute acid such as sulfuric acid, hydrochloric acid, or oxalic acid with constant agitation under controlled temperature for an extended period (a few seconds to days). Later, the nanocrystals formed by acid hydrolysis are centrifuged and washed with distilled water for neutralization of the eluent. Lastly, the suspension is mechanical stirring to obtain a homogenous suspension.[70] Rice and potato starch nanocrystals were prepared by acid hydrolysis using 3.16 M H_2SO_4 (sulfuric acid) for 5 and 7 days. The rice starch nanocrystal presented a particle size ranging from 300 to 532 nm while the potato starch nanocrystal produced by this method showed a particle size of 548-987 nm.[61] In a similar study, Velásquez-Castillo *et al.*[65] developed nanocrystals from quinoa and waxy maize starch with sizes ranging between 400 and 900 nm. In this study, acid hydrolysis was conducted in two stages, particle size of the starches was found to be 100 nm and 400-900 nm in the first and second phases respectively. As per Singh *et al.*[71] acid hydrolysis breaks the starch granules and produces starch nanocrystals with particle sizes 100-fold smaller than the native starch. Zhou *et al.*[72] demonstrated the nanocrystal synthesis from waxy maize using oxalic acid. In another study, after an acid-treatment process using sulfuric acid, the wheat starch granules were destroyed and degraded to nanoparticles with a size range of 30–80 nm.[73] Rice starch (300nm) and potato starch (548nm) nanocrystals were prepared by acid hydrolysis (3.16M sulfuric acid) for 5 to 7 days.[17]

Enzymatic Hydrolysis

Enzymatic hydrolysis is a seldom adopted method for nanocrystal synthesis from starch granules. Several enzymes are employed in the enzymatic synthesis of nanocrystals including α-amylase, β-amylase, pullulanase, and glucoamylase.[52] These enzymes target the starch granule structure which converts the amorphous region to more resistant to selective hydrolysis. Enzyme hydrolysis is also used as a pre-treatment method prior to acid hydrolysis. Pre-treatment of starch using glucoamylase reduces the duration of acid hydrolysis from 5 days to 45 hours.[74] This method is more advantageous over acid treatment as it reduces the reaction time, and increases the yield up to 55%.[75] In a recent study, nanocrystals (100-300 nm) were generated from maize, potato, and cassava starch by application of α-amylase for about 30 min.[62] Hao *et al.*[76] demonstrated the enzymatic pre-treatment (glucoamylase) of waxy potato starch prior to acid hydrolysis. The results presented a starch nanocrystal with a particle size of 80 nm. Waxy maize starch nanoparticles prepared by enzymatic treatment using pullulanase showed globular shapes with diameters of approximately 5–25 nm.[73]

Ultrasonication

Ultrasound treatment is an advanced method of processing food materials because of the low-energy consumption and less processing time.[67] Ultrasound works by cavitation phenomena during which microbubbles were generates when an ultrasound wave is introduced into the sample. It also disrupts the starch granule structure and creates pores on the surface that might act as channels for acid or enzymatic hydrolysis.[77,78] Sonication would affect the yield of nanocrystals, hydrolysis efficiency, and size which varies from 30 to 200 nm.[79] The production of starch nanocrystals using ultrasound was inspired by the synthesis of nanofibers from cellulose. Nanofibers were developed from cellulose successfully using ultrasound in several studies.[80,81,82] In a study, Liu *et al.*[83] developed nanocrystals of size 100-200 nm from debranched waxy corn starch treated with ultrasound for 5-10 min. Ultrasound-assisted acid hydrolysis was studied by Hakke *et al*.63 for the synthesis of maize starch nanocrystals (150nm). The treatment shortened the synthesis time for the formation of starch nanocrystals which is more favorable over conventional acid hydrolysis.

Dual Treatments

An effective method to generate starch nanocrystals is to apply dual treatments i.e., pretreatments with ultrasound, ball milling, or enzymatic hydrolysis followed by acid hydrolysis. Coupling of these methods is reported to enhance the efficiency of acid hydrolysis and reduce the treatment time by several folds and further the particle size.[84,85] Hakke *et al.*[63] developed oval platelet-shaped starch nanocrystals by pretreating maize starch with ultrasound (20 kHz for 20 min) followed by acid hydrolysis using 0.25 M sulfuric acid for 50 min at 30 °C. The proposed method presented a yield of 36% with an extremely low treatment time of 2 hours (reduced from 48 hours). This ultrasound-assisted hydrolysis produced nanocrystals with a particle size ranging between 50 and 100 nm.[63] In a similar study, corn starch when treated with ultrasonication and sulfuric acid generated starch nanocrystals with particle size below 100 nm. The yield of nanostarch was about 21 % and crystallinity was found to be 40%.[79] Ball milling is a cost-efficient and eco-friendly processing method that has capacity to produce starch properties.86,87 A combination of ball milling (15-90 min) and acid hydrolysis (3.16M H_2SO_4/ 40oC/5 days) has produced starch nanocrystals (19.3 %) with a short duration. The nanocrystals are found to be round-edged with an average diameter of 31 nm.88 According to Dai *et al.*[88] ball milling is observed to be a more economical and efficient pre-treatment method prior to acid hydrolysis for the production of starch nanocrystals when compared to enzymatic pretreatment or ultrasound-assisted hydrolysis. Moreover, ball milling does not require additional purification or specific instruments for mass production. Hao *et al.*[85] reported pores and cracks after enzymatic hydrolysis of waxy potato starch that created a pathway for acid penetration to produce nanocrystals (80 nm). The enzymatic pretreatment decreased the acid hydrolysis time.

Table 1. Synthesis of starch nanocrystals using different methods

Method of preparation	Starch source	Reaction tempe rature (°C)	Reaction time	Yield (%)	Particle size (nm)	References
Acid hydrolysis (H_2SO_4)	Rice and potato	40	5/7 days	-	300-987	61
	Waxy potato	40	60 days	-	276-580	89
	Quinoa	40	5 days	6.80	AHD: 243	65
Acid hydrolysis (HCl/H2SO4)	Taro and arrow root	40	3/5 days	21.64 – 40.59	10 - 938	90
Acid hydrolysis (H2SO4)	Corn	19-25	3 weeks	-	25-62	38
Oxalic acid	Waxy maize	130	15 hours	89.60	46 -197	72
Ultrasonication	Debranched waxy corn	25	5-10 min	-	100-200	83
Ultrasound + Nano precipitation	Potato	-	-	-	AHD: 74-212	91
Ultrasound + Acid						

hydrolysis (H_2SO_4)	Maize	30	70 min	-	253	63
Ultrasound + Acid hydrolysis (H_2SO_4)	Potato and maize	-	15 min (US)/ 45 min (AH)	40-80	-	53
Acid hydrolysis (H_2SO_4) + Ultrasonication	Rice	40	5 days	-	-	84
Ball milling (BM) + Acid hydrolysis (AH)	Waxy maize	40 (BM)/ 5 days (AH)	0-90 min	6.10-41.60	AHD 66-320	88
Acid hydrolysis (H2SO4) +Cross -linking	Waxy maize 130 (CL)	40 (AH) 2-6 hours (CL)	5 days (AH)	-	290-503	72
Cross-linking	Normal, high amylose waxy maize	-	1 hour	-	AHD: 35-147	92
Enzymatic hydrolysis (Pullulanase) + Supercritical Carbon Dioxide	- 60	-	-	80 to 150	93	
HMT + Acid hydrolysis (H_2SO_4)	Waxy maize	40	4 days	26.70 H: 9	D: 46	94
Enzymatic hydrolysis (α-amylase)	Maize, potato, and cassava	60	30 min		100-300	62
Enzymatic hydrolysis (Glucoamylases) + Acid hydrolysis H2SO4	Waxy potato starch	40	5 days	16.15	D: 80	85
Microwave irradiation + Nano precipitation	Waxy corn	50-100	60s	-	200-240	95

AH: Acid hydrolysis; AHD: Average hydrodynamic diameter; BM: Ball milling; CL: Cross-linking; D: Diameter; H: Height; US: Ultrasound

Characterization of Starch Nanocrystals

Globally, research has shown that starch nanoparticles can be developed from ultrasound treatment and high-pressure homogenization methods with nano-metric scale sizes and the ability to form films.[70,96,91,97] Also, several techniques have been developed to make starch nanoparticles of small size that possess high efficiency and low cost by reducing starch viscosity in aqueous paste without chemical treatment requirement.[70,97,98]

The common methods that have been used to characterize starch nano-starch are Scanning Electron Microscopy (SEM), non-contact Atomic Force Microscopy (nc-AFM), transmission electron microscopy (TEM) and dynamic light scattering (DLS). These techniques have shown the shape and dimensions of the obtained starch nanoparticles from crops such as potato and cassava starch to fit the block lets. TEM and DLS also revealed that starch nanoparticles had narrow size distribution, high dispersibility, and spherical shape.[70,51] It was also discovered that starch nano-particle films from high-pressure homogenized dispersions had lower elongation but higher tensile strength and good moisture barrier capacity and better film transparency.[70,97]

Starch nanoparticles (SNPs) have lower nano-metric dimensions in the range of 100 nm which results in better dispersion and compactness of polymeric structure.[70] Da Silva *et al.*[70] also revealed that the insertion of starch nanoparticles in a polymer leads to nano-composite producing great properties better than traditional composites.

The mechanical properties, water vapor permeability (WVP), and biodegradability of composites are improved by adding SNPs.[70] Compactness of the polymeric structure of nanocomposite films results in a decrease in the WVP making water vapor diffusion more difficult and thereby reducing permeability, however, if the reinforcement is derived from starch nano-crystals from the same material as the matrix like starch nano-crystals dispersed in starch films then better compatibilization may occur.[70] But the concentration of starch nanoparticle incorporated in a matrix polymeric need to be ascertained as lower nanoparticle concentration could result in better dispersion in the films and reduces permeability. Previous studies[70,99,100] showed that inserting less than 6% concentration of SNPs led to reduced WVP. They further observed that the use of a higher concentration of the SNPs resulted in an increase in WVP. However, this is not feasible for food packaging use because it increases the food degradation rate.[70] But water vapour permeability values are important for biofilm applications in food packaging. This is because materials that have good permeability to water vapor will be suitable for fresh food packaging and a slightly permeable biofilm will be good for dehydrated food packaging.[70,101]

Table 2: Influence of nanostarch on the properties of bio-composite films/packaging materials

S.No.	Type of starch nanocrystal	Method employed	Properties improved	Reference
1	Rice starch and potato starch	Acid hydrolysis	Reduced water vapor permeability, increased crystallinity, reduced the surface roughness and fracture	17
2	Mung bean starch	Acid hydrolysis	Reduced water vapor transmission rate, water solubility while burst strength of the packaging material increased	114
3	Waxy maize starch	Acid hydrolysis	Increased the tensile strength of the composite film on the other hand moisture content, water vapor permeability, and water-vapor transmission rate of the composite films significantly decreased	111
4	Amadumbe starch	Acid hydrolysis	Water vapor permeability of composite films decreased whilst thermal stability, tensile strength, and opacity were increased	115
5	Rice starch	Acid hydrolysis	Crystallinity and tensile strength of the film increased further improving the water barrier properties	116

SNPs have been found to increase the process of biodegradation of composites. This is attributed to the fact that water diffuses into the polymer sample in the soil resulting in swelling and biodegradation as a result of an increase in microbial.[70,102] It was found by Costa *et al.*[103] that cassava starch nano-crystals (CSN) obtained by acid hydrolysis to strengthen nanocomposite films from the same matrix with 10% CSN showed a larger weight loss due to greater microorganism access.

Starch and Other Polymer Nano-Crystal-Based Food Packaging Materials

Starch-Based Nanocomposites

Starch is a natural polysaccharide obtained from plant materials and has been used for bio-based packaging. It is a readily available, cheap, eco-friendly, and biodegradable polymer used for packaging. But its shortcomings such as low mechanical and barrier properties, and sensitivity to UV and moisture affect starch utilization.[104] Starch has been incorporated with nanoparticles like ZnO, TiO_2, Graphene, and poly (methyl methacrylate-co-acrylamide) to improve its mechanical and barrier properties.[105,106] Starch native granules are greatly affected by their sources and this makes them vary from micro to nano range (<100 µm), amorphous and semicrystalline (100–400 nm), amorphous and crystalline (9–10 nm).[107] The mechanical or barrier properties of starch have also been strengthened through chemical modifications such as acetylation and hydroxylation to replace the ester/ether group.[108,109,110] Rice starch and potato starch nanocrystals prepared by acid hydrolysis (3.16M sulfuric acid) were used in the starch-based films (Table 2). The application of starch nanocrystals in the films has reduced water vapor permeability, increased crystallinity, and reduced the surface roughness and fracture.[17] In another study, reinforcement of waxy maize starch nanocrystals in pea starch film reported an increased tensile strength of the composite film while the moisture content, water vapor permeability, and water-vapor transmission rate of the composite films decreased significantly.[111] Le Corre *et al.*[109] used acid hydrolysis of native starch as an reinforcement agent to produce starch nanocrystals.[112] Starch-based thermoplastic films have been used as food wrappers as well as for food-containing casing/crates but due to poor strength have been modified chemically or plasticized in order to improve their strength.[112]

Chitosan Based Nanocomposites

Chitosan is an abundant biopolymer which is produced from chitin, a natural polysaccharide by deacetylation of chitin. Chitosan is a biodegradable/biocompatible polymer with antimicrobial properties.[117,118] Chitosan and chitosan-based systems have been used to produce biocompatible or biodegradable films, coatings, composite materials, and nanocomposites.[118] Sriupayo *et al.*[113] used chitin sources from marine natural sources such as crustacean shells through the process of deproteinization to produce chitin nanoparticles or nanowhiskers. The process involved the use of hot alkaline KOH and then followed by hydrolysis with hot HCl under heavy stirring conditions. Chang *et al.*[118] on the other hand used a double acid treatment procedure involving the repetitive process of sonication and disruption/dispersion. Chitin nanoparticles have also been made by ionotropic gelation of chitosan with sodium tripolyphosphate.1[19] The properties of chitosan-based packaging materials have been improved by adding micro and nano-reinforcements in a polymer matrix or through the unification of chitin with other materials such as layered nanosilicates.[120,121,122.123]

Cellulose-based Nanocomposites

Cellulose is an abundant biopolymer and polysaccharide that consists of glucose monomers. Cellulose derivatives like cellulose nano-composites (CNC) are used as fillers to reinforce polymer matrices since native cellulose does not have good packaging qualities.[124,125] The incorporation of CNC improved the mechanical, thermal, and barrier properties of cellulose polymeric matrix.[126,127,128] Other forms of cellulose inserted for nano-reinforcements are nano-fibrillated and cellulose nano-whiskers.[129] Nanofibrils have a diameter in the range of 2–20 nm and examples of cellulose nano-composites are metal oxides such as Fe_3O_4, TiO_2, and metal nanoparticles like silver, and nanoclay which enhance packaging. Cellulose fibrils consist of amorphous and crystalline regions, the crystalline part is separated resulting in cellulose whiskers. Nano-whiskers are extracted by acid hydrolysis from the amorphous region which keeps the crystalline region unaffected.[130] Also, packaging films are produced from cellulose from bacteria. Although, it has a similar chemical composition as plant-based cellulose but has different properties and structures, however, it has better mechanical properties, water barrier, crystallinity, and nanofibrillar network and is therefore more preferred over plant cellulose for reinforcement.[130] Nano-reinforcement from cellulose is more important because it produced nano-composites with economical, light weighted, and better mechanical strength.

Sustainability of Starch Nano-crystals

The demand for cutting-edge, sustainable packaging materials with enhanced physical, mechanical, and barrier qualities is rising in the food business. Environmental concerns are brought up by the fact that the materials currently being used are synthetic and not biodegradable. As a result, efforts have been made in recent years to produce sustainable packaging materials consisting of bio-based components. Hence, there is an increasing interest in biobased eco-efficient and high-technology materials from starch.[131] Starch due to its biodegradability, non-toxicity, low cost, abundance in nature, and renewability, is utilized in food packaging, making it the ideal substance for the development of sustainable materials.[132] Starch nanocrystals (SNC) are crystalline nano-platelets made from the acid hydrolysis of starch which is used as nano-fillers in a polymeric matrix. SNC preparation process is being scale-up due to new applications of starch nanocrystals. But the sustainability of this new bio-based nano-material will depend on its preparation and processing as well as its impacts on the environment.[113] On the other hand, starch films that are filled with starch crystals showed greater UV protection. It is not only biodegradable but also suitable for food packaging. It may also be used to develop edible films as they are obtained from food sources.[133] Foam materials produced using cassava starch showed a considerable biodegradation of over 50% after 15 days in the biodegradation test. The results of the study imply that the dual-modified cassava starch-based biodegradable foams have promise for substituting petroleum-based materials in sustainable packaging applications.[134]

Polysaccharides have semi-crystalline structures which offer a great opportunity for the preparation of biobased nanoparticles. Starch is a polysaccharide that is abundantly produced by plant resources. Starch nanocrystals could be prepared by disrupting the starch granules by acid hydrolysis of amorphous parts. Lab-scaled SNCs have been produced with different morphologies with individualized platelets.[113]

Safety and Regulation of Nanomaterials in Food Packaging

Although the application of nanoparticles in food processing and packaging has advanced significantly, little is known about the toxicity of these materials. Nanoparticles are currently being applied in food products at a rate faster than desired, posing a risk to the environment and human health.[135] Nanoparticles present in food packaging can enter the respiratory systems of employees and can be exposed to it through the digestive system. Any nanoparticles that enter the respiratory tract are cleared by the mucociliary system before entering the digestive system. Any nanoparticles that penetrate the respiratory tract make their way through the digestive system through mucociliary clearance that will cause serious illness and may sometime be life-threatening.[136]

Hence, it is important to research every aspect of nanoparticle toxicity and environmental behaviour. The effects of food processing and packaging systems based on nanotechnology on human health should be taken into consideration by food regulations. A regulatory framework that can control any risks associated with nanofood and the use of nanotechnologies in the food business is urgently needed. Also, governments must address the broader economic, social, ethical, and civil rights concerns brought on by nanotechnology. Public engagement in decision-making about nanotechnology is essential to ensure the democratic management of these technological advancements in the key domain of agriculture and food.[137] In 2011, the European Food Safety Authority (EFSA) published a directive titled "on the risk assessment of the application of nanoscience and nanotechnologies in the food and feed chain,[138] outlining the physicochemical information that the manufacturer must submit. Considering the challenges to accurately measure and categorize nanomaterials, EFSA does not explain how these standards might be reached in a consistent and economical way.

Limitations of Starch Nanocrystals in Food Packaging

Nanotechnology has been reported to possess great potential for food packaging applications. Nevertheless, a few limitations were noted, including the possibility that products containing nanomaterials may perform novel functions for which it may be challenging to compare them to more traditional functional alternatives, the potential difficulty of developing an inventory due to rapidly evolving production technologies, or the difficulty of assessing the risks associated with nanomaterials due to the dearth of information on their release, exposure, and effects.[135,136]

Conclusion

Consumer demand for varieties of food has increased research into the development of more reliable, effective, safe, and eco-friendly food packaging. Nanotechnology as an emerging field has been a source of hope in developing food packaging with improved physical, mechanical, and functional properties. Polysaccharides are major sets of natural biocompatible or biodegradable food packaging materials that could turn around the production of nanocrystals for food packaging applications. Starch which is a most abundant natural biological macromolecule which has great industrial applications, particularly in the packaging sector. Acid hydrolysis is the most predominant method used for the synthesis of starch nanocrystals. Dilute acids such as sulfuric acid, hydrochloric acid, or oxalic acid were widely used in nanostarch synthesis. The starch nanocrystals synthesized by acid hydrolysis presented an improved mechanical, water barrier, oxygen barrier, and antimicrobial properties of packaging materials and further enhanced the shelf life of the food products. The major limitation of nanotechnology is its complexity in assessing the risks associated with nanomaterials due to the dearth of information on their release, exposure, and effects. The next generation of food packaging will come from biodegradable polymeric materials from nanostarch to give eco-friendly packaging however its toxicological studies should be carried out extensively in the future.

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Conflict of Interest

The authors do not have any conflict of interest.

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