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Starch nanoparticles for food packaging applications: A Review

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ABSTRACT

Starch is one of the most used biodegradable polymers for food packaging applications. It has suitable properties and characteristic in the development of sustainable materials, including the biodegradability, non-toxicity, affordability, natural abundance, and renewability. The development of starch materials in form of nanoparticles has become more attractive due to its capability to functionalize with bioactive compound in forming of functional packaging materials. It also can be used as nanofillers to enhance the mechanical and barrier properties of bio-composite materials for food packaging materials. This article provides a short review of the development starch-based nanoparticles for food packaging applications.

ABSTRAK

Pati merupakan polimer biodegradable yang paling banyak digunakan untuk aplikasi kemasan makanan. Polimer ini memiliki sifat dan karakteristik yang paling sesuai dalam pengembangan material berkelanjutan, diantaranya kemampuan biodegradabilitas, non-toksisitas, ketersediaan, dan dapat diperbarui kembali. Pengembangan material pati dalam bentuk nanopartikel menjadi lebih menarik karena kemampuannya memfungsionalisasi senyawa aktif menjadi material kemasan yang fungsional. Pati juga dapat digunakan sebagai nano-filler untuk meningkatkan sifat mekanis dan penghalang material biokomposit pada material kemasan makanan. Artikel ini akan mengulas perkembangan nanopartikel berbahan dasar pati untuk aplikasi kemasan makanan.

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1. Introduction

Plastics have been the most frequently utilized materials for food packaging applications due to their low production costs, greater adaptability, strong water and gas permeability barrier qualities, as well as their mechanical and optical properties [1]. However, plastic usage as packaging material has a particularly negative impact on the environment. It has high durability and slow decomposition for up to 400 years [2]. Hence, it has become more necessary to replace plastic usage by using biodegradable materials in food packaging applications.

Biopolymers have been proposed as an alternative material to replace synthetic plastic. It offers similar characteristic as synthetic plastic, yet they have less biodegradation time, good biocompatibility, and high availability [3]. Carbohydrates and protein are the most widely used compounds to produce biopolymers which then be used for the industrial production of food packaging materials [4].

The most prevalent carbohydrates in nature are polysaccharides, which may be found in a wide variety of organisms including plants, animals, and microorganisms. Polysaccharides are appropriate for use in food packaging due to their inherent qualities of biodegradability, biocompatibility, and nontoxicity[5, 6]. Starch, cellulose, chitin, chitosan, alginate, and hyaluronic acid are among the polysaccharides that are most frequently utilized in food packaging [4, 6].

Starch is a natural polymer composed of amylose and amylopectin. It can be obtained based on grains, vegetables, or fruits. The use of starch in many applications is still very limited because of its physical and chemical properties. Thus, it needs to be modified to enhanced the characteristic and properties of starch compound. The use of nanoparticles technology in food packaging is currently considered to be a promising area to enhanced the functionality of starch as packaging materials.

Although there are a number of reviews about preparation and applications of polysaccharides based macro/nanoparticles for food packaging materials [6, 7], including polysaccharides-based nanocomposites for food packaging applications [8-10], only few reviews addressed the literature on starch-based nanoparticles from the perspective of preparation method and particular application, e.g. food packaging applications [11, 12]. This review intends to summarize the studies of preparation and processing method of starch-based nanoparticles for food packaging applications. The development of starch materials in food packaging applications is highlighted in section 2, while various preparation methods are discussed and reported in section 3. The application of starch-based nanoparticles are discussed in section 4 and round off with a conclusion and future perspective of starch-based nanoparticles roles in the food packaging industry.

2. Starch in Food Packaging Applications

Starch is a glucose homopolymer with α-glycoside bonds, which are found in plants nainly in seeds and roots [12]. In its original form, it is a small particle called a granule. It consists of two main components, amylose and amylopectin. Different type of starch consists different ratio of amylose and amylopectin. Furthermore, the characteristics of starch are influenced by the botanical source, the shape and size of starch granules, ratio of amylose and amylopectin, the content of non-starch compounds, and crystalline-amorphic structures [13]. The particle size of starch is normally ranging from 0.1 – 200 μm with various morphologies, including oval, ellipsoidal, spherical, fine, and lenticular [8].

Starch has gain popularity to be used as raw material in food technology application due to its availability, biodegradable, and uniquely granular properties [13]. It has been reported by Krochta, et.al in 1994 that starch based edible film has many advantages compare to synthetic plastic materials, including biodegradable properties, aesthetic appearance, edible, and its ability as an oxygen barrier during food transport and storage [14] . Polysaccharide edible film can serve as permeable membrane during the exchange of O_2 and CO_2 gases so it can lower the level of respiration in food.

The development of starch-based materials for industrial application can be divided into three periods: traditional, transitional, and nanostructured (fig. 1). In traditional period, the invention of starch as thermoplastic materials has begun. The preparation of starch-based thermoplastics was conducted by using extrusion, foaming processing, film casting, and flow technologies. Further, the modification of starch-based materials was initiated in transitional era in order to improve the physical and chemical properties of starch. For examples, starch can be incorporated into another hydrophobic polymer to increase its hydrophobicity.

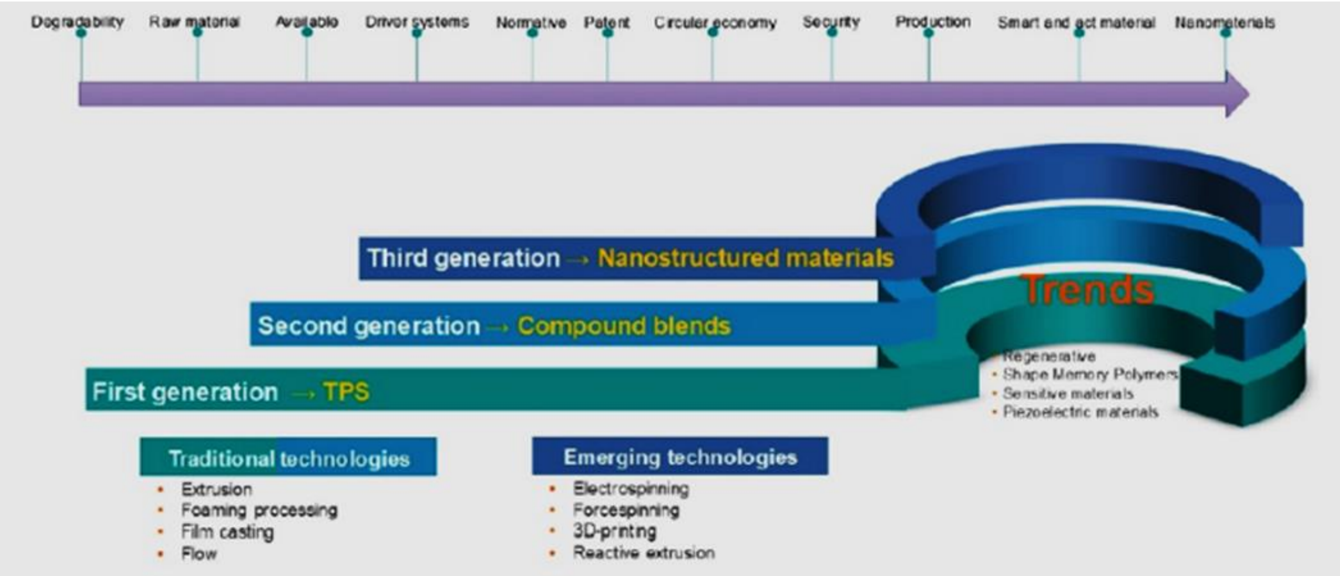

Figure 1. Development process of starch-based materials in food packaging applications [7], Copyright © 2022 by MDPI. Reprinted by permission of MDPI

In order to transform starch into thermoplastic material, the modification process was conducted by adding plasticizers such as water, glycerol, and other polyols. The transformation also can be obtained via heating process under temperature of 90-180 °C. It will initiate gelatinization process followed by the arrangement of crystalline structure and form the unstructured starch. As a result of this process, poor mechanical and hydrophilic properties are present, which make it unsuitable for food packaging application. Further modification, including chemical modification and polymer blending, become necessary to improve starch's properties and reduce the flaws in starch-based materials.

Currently, the modification and processing techniques of starch-based materials has been achieved the most advanced at nano-scale level to obtain high performance starch materials. Some studies have shown that nanotechnology can increase the properties of packaging materials, including tensile strength, moisture barrier, and antibacterial properties [15]. Starch-based nanomaterials can also be used as catalysts for antioxidants, which will enhance the shelf life of food.

3. Synthesis of Starch Nanoparticles

Starch nanoparticles, also known as nano-sized starch particles or nanocrystalline starch, refer to starch molecules that have been reduced to very small dimensions on nanometer scale. Starch nanoparticles have been identified as amorphous particles with larger particle size compare to starch nanocrystals. Nevertheless, in some context both starch nanoparticles and starch nanocrystals have been considered as the same objects in term of their crystalline components. Recently, starch nanoparticles have gain many attentions due to their great opportunity to be produced in mass scale production, abundant availability, renewability, biodegradability, non-toxicity, and biocompatibility properties [13]. Another advantage is the ability of starch nanoparticles to preserve active compounds via encapsulation process [16]. Encapsulated starch nanoparticles can control the release of active compounds, improve stability of active compounds, and enhanced functional properties of food materials [17] [16].

There are variety of methods that can be used to produce starch nanoparticles, including hydrolysis using acid, extrusion, emulsification, and nanoprecipitation. These processes break down the larger starch molecules into smaller particles with sizes typically ranging from 10-1000 nanometers. The resulting nanoparticles possess unique properties and characteristics that differ from those of conventional starch.

The synthesis of starch nanoparticles typically involves two main methods: top-down and bottom-up approaches [18]. The top-down approach involves breaking down bulk starch into smaller size through mechanical or chemical methods. Meanwhile, the bottom-up approach involves synthesizing starch nanoparticles from smaller particles building blocks (Figure 2).

In top-down approach, the starch initially isolated from the plant source followed by gelatinization process to disrupt the starch granules [12, 19]. Gelatinization process is conducted by heating the starch in the presence of water. Furthermore, the mechanical or chemical methods are applied to break down the gelatinized starch into smaller particles. After the mechanical or chemical treatment, starch suspension is subjected to purification process to separate the nanoparticles from larger particles and impurities. At final process, the starch nanoparticles will be dried, commonly by using freeze-drying or spray-drying method to obtain a powder form for further use.

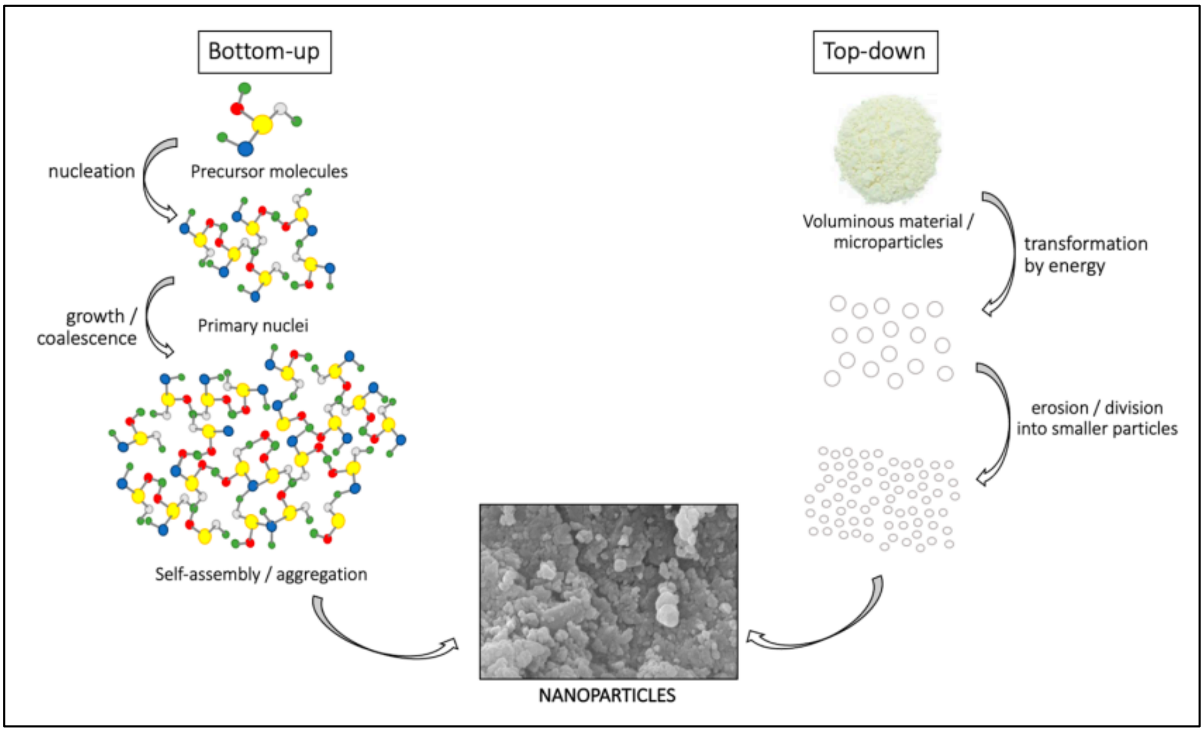

Figure 2. The preparation methods of starch nanoparticles [20], Copyright © 2021 by MDPI. Reprinted by permission of MDPI

Most common method to synthesize starch nanoparticles via bottom-up method is acid hydrolysis [18]. The formation of starch nanoparticles involves synthesis process from small particles building blocks. Starch solution was prepared by dissolving starch powder in water followed by treating the solution to create acidic condition through the addition of acid compound such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl). The addition of acid will induce the formation of starch's small fragments through hydrolysis process. Base solution then added into starch solution in order to terminate the hydrolysis reaction. The purification process will be conducted to remove excess acid or base solution and soluble by products by performing dialysis process. The purified starch nanoparticles in form of powder will obtain after drying session by using freeze-drying or spray-drying methods. Different methods of starch nanoparticles preparations are presented in Table 1.

Table 1. Different methods of starch nanoparticles preparation

Source of starch	Method	Synthesis processing condition	References
Native sago starch	Precipitation	The NaOH/urea (NU) (0.8:1 wt%) for solution based, absolute ethanol (10 mL, 15 mL and 20 mL) as oil phase, stirred at room temperature, 30 min.	[21]
Potato starch	Acid hydrolysis	Solution of sulphuric acid, 7 days at 40 ◦C.	[22]
Horse chestnut, Water chestnut, and Lotus stem	Mild alkali hydrolysis and ultra-sonication process	Solution of 0.1M NaOH, 30 min at 80 °C , sonicated at 40 KHz for 30 minutes at intervals of 5 minutes.	[23]
Waxy maize	Self-assembly	100 mL of disodium hydrogen phosphate and citric acid buffer solution (pH 4.6), in boiling water for 30 min to fully gelatinize the starch, stirred at 58 °C. 400 mL of absolute ethanol were added, stirring at room temperature.	[24]

The characterization is required in order to understand the structure, size, morphology, and functional properties of starch nanoparticles. It is essential to have the information of their physicochemical properties so it can be applied in specific applications of various industries. The size, structure, and characteristics of the produced starch nanoparticles can be examined using a variety of characterization techniques, including electron microscopy, dynamic light scattering, X-ray diffraction, and Fourier-transform infrared spectroscopy.

Scanning Electron Microscopy (SEM) is used to visualize the morphology and size distribution of starch nanoparticles. It provides high-resolution images, allowing researchers to observe the shape, surface features, and aggregation behavior of the nanoparticles. Transmission Electron Microscopy (TEM) provides detailed information about the internal structure of starch nanoparticles. It enables visualization of the crystalline regions, amorphous regions, and surface properties at a nanoscale level. TEM can also be used to measure the particle size and aspect ratio. The example of starch nanoparticles' SEM micrograph has shown in figure 3 below.

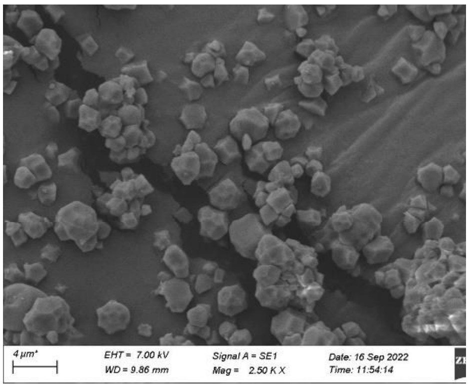

Figure 3. SEM micrograph of starch nanoparticles [17]

Another characterization analysis is X-ray Diffraction (XRD), which is used to determine the crystallinity and crystal structure of starch nanoparticles. By exposing the nanoparticles to X-ray radiation, the resulting diffraction patterns can be analyzed to identify the crystallographic phases and calculate the crystallinity index. Fourier Transform Infrared Spectroscopy (FTIR) commonly used to study the chemical composition and functional groups present in starch nanoparticles. It provides information about the molecular structure, such as the presence of amylose and amylopectin, as well as any modifications or interactions with other substances. Dynamic Light Scattering (DLS): DLS is used to measure the size distribution and particle size of starch nanoparticles in solution. By analyzing the intensity fluctuations of scattered light caused by the Brownian motion of the nanoparticles, DLS provides information about the hydrodynamic diameter and polydispersity of the particles. All these techniques, along with other analytical methods, help researchers understand the physicochemical characteristics of starch nanoparticles and optimize their properties for various applications.

4. Starch-based Nanoparticles for Food Packaging Applications

In food packaging application, starch nanoparticles have been used as packaging materials in form of edible film or coating to enhance food shelf-life. Another application of starch nanoparticles is the employment as nano-filler in food packaging materials [25]. It has been reported in some studies that starch nanoparticles can control the oxidation of food and prevent the formation of undesirable food flavors and textures [26]. Stach nanoparticles also commonly used as reinforcing materials in bioplastic, to improve the properties of bioplastic including the mechanical properties, enhanced plastic degradability, and limiting the permeability of oxygen and water [26-28].

Some studies also reported the utilization of starch nanoparticles as antimicrobial agents in food packaging applications [29-31]. Starch nanoparticles can provide large surface area as compartment of active substance which allow the grow of particular microorganism and increases antimicrobial efficiency [32]. In nanocomposite manufacturing process, the presence of starch nanoparticles can reduce the bacterial resistance by decreasing the overall pore size of composite film [33]. These studies have shown that starch nanoparticles can improve food safety as antimicrobial agents in food packaging. Different potential applications of starch nanoparticles food packaging are presented in Table 2 below.

Table 2. The applications of Starch Nanoparticles for food packaging applications

Materials	Applications	References
Waxy maize SNPs	Decrease in water vapor permeability of sorbitol-plasticized pullulan film	[34]
Cassava SNPs	Decrease in the permeability by 40% for a cassava starch film	[35]
Waxy maize SNPs	Reduce the oxygen diffusion and permeability of a nanocomposite film pre-pared with natural rubber (NR)	[36]
Cassava SNPs	Antimicrobial biodegradable packaging	[37]

5. Conclusions

Starch-based nanoparticles have shown promising potential to be used as biobased-packing materials, particularly in food packaging applications. These materials offer several advantages for food packaging applications, including biodegradability, compatibility, antimicrobial properties, and food safety. Further studies are still required to solve the environment issues due to mechanical and physical properties of starch-based nanoparticles for food packaging applications.

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