Review

A comprehensive review of polysaccharide-based bionanocomposites for food packaging applications

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Abstract

The newly engineered functional systems of nanotechnology implemented in food packaging minimize food product loss by extending shelf life. The incorporation of nanostructured materials into packaging formulations enhanced the existing characteristics of food packaging materials by increasing the specific surface area of these biopolymers. Natural biopolymers were regarded as greener, more sustainable, and environmentally friendly materials. Starch nanocrystals have been employed effectively as fillers in polymer matrices to enhance mechanical and moisture barrier characteristics. Both chitin and chitosan nanoparticles were biocompatible, biodegradable, inexpensive in cost, and mucoadhesive in nature. Alginate nanoparticles demonstrated high thermal and chemical stability. Because of these features, polysaccharide-based nanoparticles were excellent candidates for nano reinforcements in bio-nanocomposites. The nano sized forms of starch, chitin, chitosan, and alginate are non-toxic and antimicrobial. This study focused on current advances in the development of food packaging films based on starch, chitin, chitosan, and alginate nanoparticles, as well as trends and challenges in the formulation of bio-based polymers. This review detailed the synthesis of starch, chitin, chitosan, and alginate nanoparticles using various techniques such as hydrolysis, ionic gelation, reverse micellization, emulsification, and crosslinking. This type of polysaccharide-based bio-nanocomposite is expected to revolutionize the entire food packaging industry.

Keywords Nanotechnology · Food packaging · Chitin · Starch · Chitosan · Alginate · Ionic gelation · Crosslinking

1 Introduction

The primary role of food packaging is to protect the product and maintain its shelf life. The food contained within the package should be safe and of acceptable quality. The food industry is continually searching for new technologies to improve and promote additional packaging aspects, such as traceability, microbial growth prevention, and food safety. The application of nanostructured materials in packaging materials can improve the existing qualities of food packaging materials [1]. Nanostructured materials are those in which the structural constituents have at least one dimension in nanometric scale and the diameters ranging from 1 to 100 nm. Nanostructured materials include nanoparticles, nanorods, nanowires, thin films, and bulk materials made from nanoscale building blocks or containing nanoscale

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features. Nanostructured materials are categorized as zero-dimensional (nanoclusters, quantum dots, fullerenes), one-dimensional (nanorods, nanotubes), two-dimensional (ultrafine-grained over layers, thin films), or three-dimensional (particles, nanocomposites, dendrimers) nanomaterials. Nanotechnology has paved the way for the use and development of novel nanostructured materials known as nanomaterials in the food packaging sector.

The packaging system provides protection, containment, distribution, transportation, and identification of food materials along the supply chain from farm to fork. The conventional materials used in food packaging are non-biodegradable petroleum and plastic polymers, leading to severe effects on the global environment. As a result, the usage of biodegradable packaging materials made from recyclable resources can minimize environmental consequences while increasing waste utilization from agro-based sectors. Agriculture and food product wastes are examples of biodegradable waste, from which materials such as polysaccharides, cellulose, silica-based materials, etc., can be obtained and utilized in the production of nanomaterials for food packaging systems. Therefore, nanomaterials based on naturally derived polymers can increase the quality of biodegradable and edible food packaging materials, which are considered more environmentally friendly than that other traditional packaging films [2].

The quality and freshness of the product are maintained in the time of commercialization and consumption by an accurate selection of packaging material and technology. Incorporating nanoparticles into polymer matrices can assist in maintaining these properties in food packaging materials [3]. Nanomaterials provide a range of functional characteristics in the packaging, such as improving thermal, barrier, and mechanical properties. Therefore there is a growing need for nanomaterials in food system packaging. Nanomaterials are used in food items to modulate the release of antioxidants, flavors, enzymes, and antimicrobials [4]. Nanomaterials included in food packaging materials release active ingredients in a regulated manner and prevent food spoiling [5]. As a result, nanomaterials in food packaging enhance the usage of biodegradable materials in packaging, reduce wastage of processed foods, preserve food freshness, and increase shelf life [6, 7].

Polysaccharides are abundant are the most abundant carbohydrates in nature and can be obtained from plants, animals, and microbes. Polysaccharides have intrinsic properties such as biodegradability, biocompatibility, and non-toxicity, making them suitable for use in food packaging. Polysaccharides are large, high-molecular-weight compounds generated by glycosidic bonds connecting monosaccharide units. The various natural biopolymer for the formation of bio nanocomposites for food packaging applications are presented in Fig. 1. The most common polysaccharides used in food packaging include starch, cellulose, chitin, chitosan, alginate, and hyaluronic acid. These polysaccharide-based nanoparticles can be used as fillers to improve the physical properties of biopolymers.

The application of bio-nano composites in industrial packaging is being researched as part of the continuous quest for novel solutions for efficient and sustainable systems. Bio-nanocomposites are eco-friendly components made from biodegradable and renewable material and hence referred to as green nanocomposites. Bio-nano composites have anti-bacterial characteristics that allow them to inactivate bacteria more efficiently due to the increased surface-to-volume ratio and higher surface reactivity of the nanosized antimicrobial agents. On this basis, this review was conducted on the synthesis of polysaccharide (starch, chitosan, chitin, and alginate) nanoparticles and the development of bio-nano composites integrating polysaccharide-based nanoparticles into the biopolymeric matrices. The techniques for the synthesis

Fig. 1 Various natural biopolymer for the formation of bionanocomposites for food packaging applications
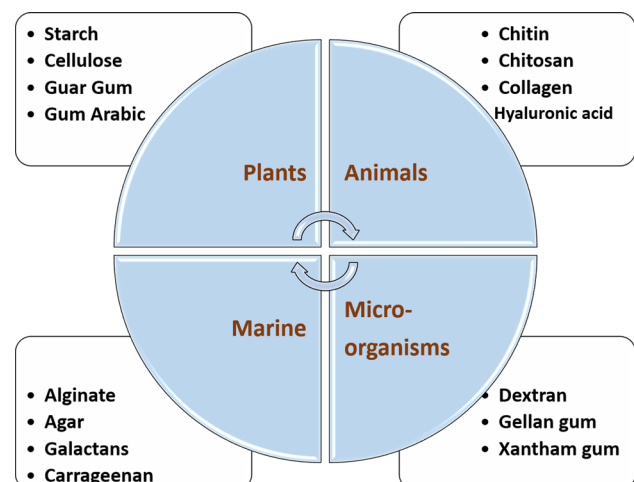
of starch, chitosan, chitin, and alginate nanoparticles and their applications for enhancing the properties of packaging films are covered in this review.

2 Type of review and search strategy

This review addressed the literature on polysaccharide-based bionanocomposites in an integrated manner, allowing for developing novel frameworks and perspectives on the theme. In order to improve the understanding of the phenomenon of bionanocomposites, this review combines both experimental and theoretical research conducted in the area. Different databases were used to arbitrate various intellectual studies, including journal articles, conference proceedings, and books. To ensure adequate and efficient coverage of the research topic and literature review, databases such as Scopus, Web of Science, and Google scholar were used for the searches. A few of the search strategy strategies used were online searching with keywords, specific phrases, and subject headings. A bibliographic approach strategy was used in this review for the literature search.

3 Polysaccharide-based nanoparticles for food packaging

Polysaccharide-based NPs are made from natural biomaterials like polysaccharides, decreasing toxicity, biodegradability, and physiological stability concerns. Polysaccharides are abundant in nature, making them low-cost biomaterials to investigate. This review discusses the synthesis and application of starch, chitin, chitosan, and alginate nanoparticles in food packaging films. The different methods of preparation of polysaccharide nanoparticles are presented in Fig. 2. Starch-based nanosystems are frequently classified into two types such as starch nanocrystals and starch nanoparticles. A number of processes, including acid or enzymatic hydrolysis and physical disintegration, can be used to create starch nanocrystals and nanoparticles. The acid hydrolysis process yields starch nanocrystals with high crystallinity and a platelet-like shape by hydrolyzing the amorphous component of the starch granules. Starch nanoparticles are completely amorphous particles produced by controlled nanoprecipitation of gelatinized starch. It has been observed that starch nanoparticles have larger particle sizes than starch nanocrystals and that their size and shape may be adjusted by the synthesis procedure in both situations. In several contexts, starch nanoparticles and starch nanocrystals are considered synonymous since both terms relate to the crystalline components of starch that remain after hydrolysis or other physical treatments. Starch nanocrystals and nanoparticles have been employed effectively as fillers in polymer matrices to improve mechanical and barrier characteristics. Different methods of preparing starch nanoparticles from various starch sources are presented in Table 1.

3.1 Starch nanocrystals

Starch nanocrystals are semi-crystalline platelets of starch granules formed by hydrolysis with sulfuric acid in amorphous areas. They have different sizes depending upon the source of starch; e.g., the sizes of starch nanocrystals obtained from potato starch, pea starch, and maize starch are 40–70 nm, 60–150 nm, and 70–100 nm, respectively [8]. Hydrolysis of nanocrystals is usually performed below gelatinized temperature. The size and yield of starch nanocrystals are highly affected by the conditions of hydrolysis during the extraction process. The structure and morphology of starch nanocrystals are mainly determined by crystallinity and the relative proportion of amylose and amylopectin content. Starch nanocrystals are used as filler components in polymeric matrices to increase the tensile strength of packaging film. Starch nanocrystals also reduced the oxygen transfer rate and water vapor permeability of packaging film. The addition of 5% maize starch nanocrystals produced by acid hydrolysis to pea-starch films enhanced tensile strength by around 72% [9]. The inclusion of starch nanocrystals had a significant influence on the characteristics of Polycaprolactone, increasing the tearing strength from 37 to 45 kN/m and decreasing the oxygen transmission rate from 1740 to 1250 cm^3 /m^2 day [10]. The inclusion of 5% starch nanocrystals to mango kernel starch films enhanced the tensile strength by around 90% and elastic modulus by 120% while lowering the water vapor permeability by approximately 15% [11]. There are three methods that are used to synthesize nanocrystals, which include (i) hydrolysis, (ii) the Regeneration/ nanoprecipitation process, and (iii) physical methods.
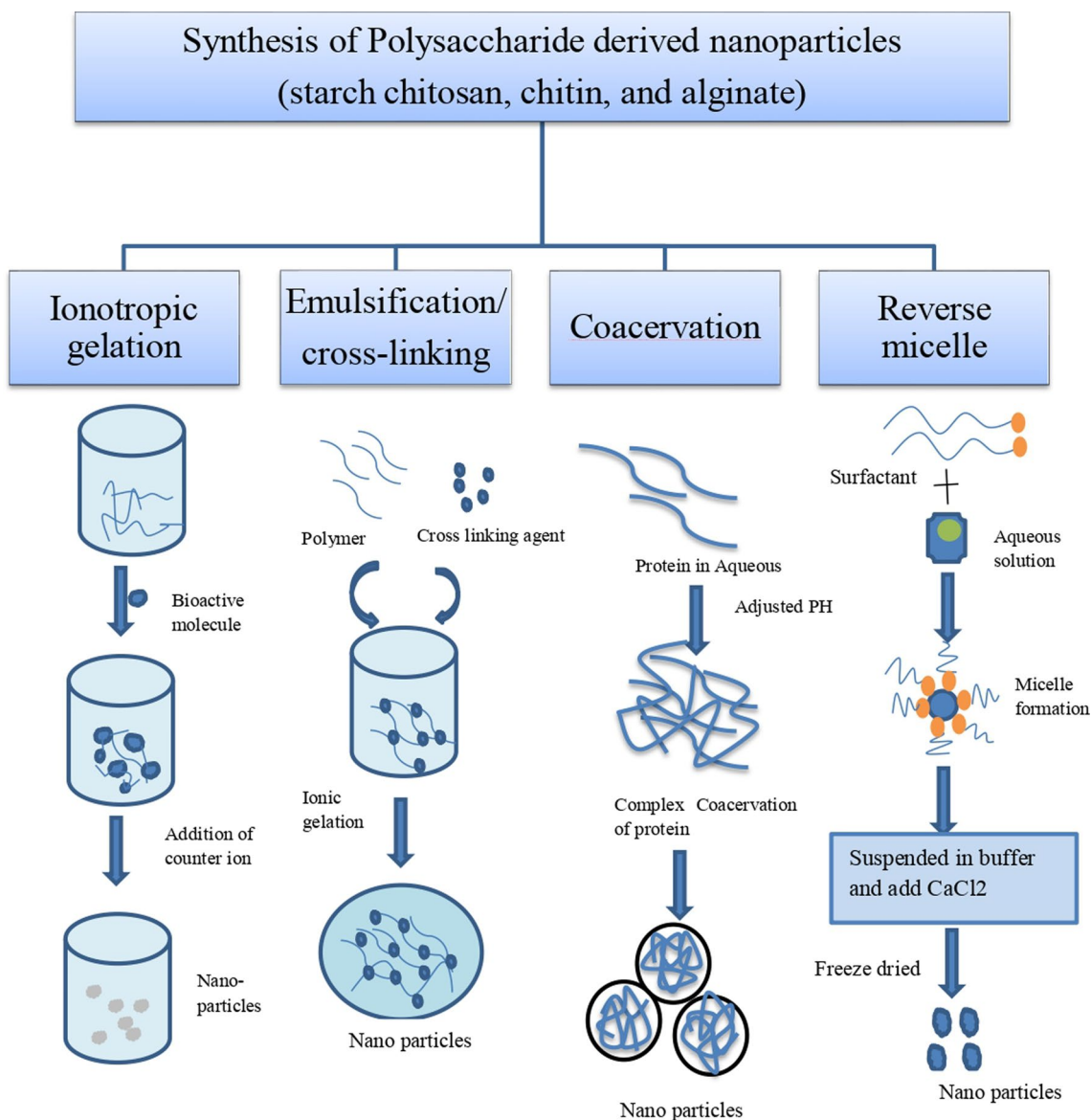
Fig. 2 Method of preparation of polysaccharide nanoparticles

3.1.1 Hydrolysis method for starch nanocrystals

3.1.1.1 Acid hydrolysis A method commonly used to create starch nanocrystals is acid hydrolysis. There are two stages of acid hydrolysis in starch nanocrystal formation: the first stage involves hydrolysis at a very fast rate, and in the second stage, the rate of hydrolysis is slow, while some studies have proven that acid hydrolysis is completed in three stages: rapid, slow, and very slow. Rapid hydrolysis attacks amorphous parts of the granule of the starch, while as slow hydrolysis involves erosion of the crystalline regions [12]. Acid hydrolysis involves dilution of starch by hydrochloric or sulfuric acid with continuous stirring for a long time under controlled temperature followed by centrifugation and washing with distilled water for differentiation of starches from acid. Starch nanocrystals developed by acid hydrolysis possess high crystallinity. To isolate the crystalline regions from starch granules, acids such as sulfuric acid or hydrochloric acid are used at low temperatures, usually below the gelatinization temperature. Low temperature prevents starch breakdown and starch gelatinization. There is rapid hydrolysis in the amorphous regions compared to crystalline regions [13]. After acid hydrolysis, the residue comprises highly crystalline nanocrystals with nanoscale morphology. The acid hydrolysis process is affected by the type of acid and the duration of the hydrolysis. Some studies have revealed that 15 days require hydrolysis by HCl, while seven days are required for H_2SO_4 [14].

Table 1 Different methods of preparation of starch nanoparticles from various starch source

Source of starch	Preparation method	Condition for making nano starch	References
Waxy corn starch	Acid hydrolysis	2.2 mol/L HCl at 36 °C for 40 days 3.16 mol/L H_2SO_4 at 40 oC for 5 days	[31]
Corn starch	Acid hydrolysis	2.87 mol/L H_2SO_4 at 45 oC for 7 days	[32]
Pea starch	Acid hydrolysis	3.16 mol/L H_2SO_4 at 40 oC for 5 days	[33]
Potato starch	Acid hydrolysis	2.2 mol/L HCl at 36 °C for 15 days	[34]
Corn + pullulanse	Precipitation	2.2 N HCl solution in the ratio of 1:2, heated 12 h Neutralization with 1 N NaoH	[35]
Banana + aloe vera	Precipitation	Ph maintained at 2.0, 3.0,4.0 and 5.0 Incubation time: 40, 60, 80 and 100 oC Temperature: 100 oC	[36]
Quinoa	Precipitation	2.2 N HCl solution in the ratio of 1:2, heated 12 h Neutralization with 1 N NaoH	[35]
Quinoa and maize	Ultrasounds	Power: 100 W 30 cycles of sonication for I mint	[36]
Araucaria angustifolia	Ultrasounds Acid hydrolysis	Power: 100 W 30 cycles of sonication for I mint 2 ml/100 ml HCl for 50 days at 22 oC	[36]

Response surface methods were used to optimize the conditions of acid hydrolysis to form starch nanocrystals and optimize the impact of acids and the final yield of nanocrystals [15]. It was observed that sulfuric acid hydrolysis produces starch at a large scale compared to HCl hydrolysis, which produces different starch nanocrystals with low yield quality and takes maximum time to complete the process. It also has less potential to be utilized as a nanofiller. The concentration of acid, acid type, time, and temperature are the main conditions affecting hydrolysis, while the source of starch also affects hydrolysis. The kinetics of hydrolysis is affected by the type of acid and source of starch and divided kinetics into two steps: Step 1 involves hydrolysis at a fast rate, while in step 2, hydrolysis is completed at a slow rate [16]. The stability and distribution are increased due to sulfate formation but reduce the thermal stability of nanocrystals by using the H_2SO_4 hydrolysis method. Therefore, adding 0.5% ammonia (0.5%) to H_2SO_4 starch slurry prior to centrifugation enhances the thermal stability of the nanocrystals [17].

3.1.1.2 Enzymatic hydrolysis Enzymes such as α-amylase, β-amylase, and glucoamylase are utilized to synthesize starch nanocrystals. It was suggested that utilization of the α-amylase enzyme for hydrolyzing natural starch at 37 °C for 24 h at 150 rpm formed starch nanocrystals with a size of 500 nm [18]. α-amylase hydrolysis separates the amorphous regions present in the starch granules. Ultrasonication was used to provide stability in the resultant product. Potato starch, pea starch, waxy corn starch, and corn starch are some common sources of starch used to make nano starch crystals by enzyme hydrolysis [19].

3.1.1.3 Combined enzymatic and acid hydrolysis Both acids and enzymes together can be used in the development of starch nanoparticles, which reduces the duration of acid hydrolysis. Pretreatment with enzymes provides the path for acid to penetrate in granules, leading to easy hydrolysis of the amorphatic region. A two step kinetic process is followed by combined hydrolysis. Pretreatment of enzymes before 2 h of acid hydrolysis decreased the hydrolysis time from 23 to 5 h [20].

3.1.2 The regeneration/nanoprecipitation process

Nanoprecipitation is a method commonly used for the synthesis of amorphous starch nanoparticles. The process involves gelatinization of starch prior to precipitation. Starch nanocrystals were formed by nanoprecipitation, and the crystallinity was maintained through selective enzymatic hydrolysis [15]. Maize starch with a suspension of high amylose was heated in a water bath in 90% dimethyl sulfoxide (DMSO) for 24 h at 35 °C followed by filtration, in which the filtration device was divided into two parts in which one part was filled with an exact amount of starch and another with butanol. The apparatus was placed in a heated air oven at 70 °C for six days, followed by the collection of the precipitate centrifugation of the suspension and washing three times with n-butanol. The yield obtained from this process was very low,

as the maximum amount of starch was hydrolyzed during this process [21]. In another study, starch nanocrystals were synthesized by using the nanoprecipitation technique by using absolute ethanol for precipitation. The mixture of NaOH and urea is used as a solvent for the dissolution of starch. A gently measured amount of absolute ethanol was added and stirred, followed by centrifugation, washing with ethanol, and then the collection of starch nanoparticles [22].

3.1.3 Physical methods for starch nanoparticle/starch nanocrystal development

3.1.3.1 Reactive extrusion The physicochemical and structural properties of starch are altered by subjecting it to the highest pressure, temperature, and shear [23]. The first patent was filed to prepare starch nanoparticles through a process called reactive extrusion using a twin-screw extruder that produces particles less than 400 nm in diameter. Another study was conducted in which starch nanocrystals were prepared by reactive extrusion utilizing a cross-linking agent, and the size of the nanoparticles obtained was 160 nm [24].

3.1.3.2 High-pressure homogenization Preparation of starch nanocrystals by high-pressure homogenization is an easy and eco-friendly method discovered by Liu and others in 2009. A homogenized slurry of starch is passed constantly through a microfluidizer. A reduction in particle size was observed from 5 μm to 10–20 nm when starch suspensions of 5% were allowed to pass under pressure [25]. Starch nanocrystals have also been prepared combining cross-linking and high-pressure homogenization [26]. Another combination of homogenization and heat moisture developed nanocrystals yielding 80% final product with a diameter of 50 nm [15, 27].

3.1.3.3 Using gamma radiation Gamma radiation is also used for the production of starch nanocrystals. This radiation will lead to cleavage of glycosidic linkages in starch, leading to the fragmentation of larger molecules at a very rapid rate. Free radicals are formed because small molecules such as dextrins are produced by the breakage of chemical bonds in starch. These starch nanocrystals produced from this process are vulnerable to heat degradation in comparison to natural starch [28].

3.1.3.4 Ultrasonication Sound waves within the frequency range of 15–20 kHz are known as ultrasounds, and these waves are above human hearing. Ultrasonication was used to prepare starch nanoparticles derived from waxy maize starch suspensions. It was performed in a water bath at 8 °C for 75 min. The results obtained from SEM showed that the limiting size of starch nanocrystals obtained by ultrasonication was 30–100 nm. Parameters such as the concentration of starch, source, time, and temperature, as well as the power of sonication, affected the process of ultrasonication on starch [29]. Ultrasonication was used to synthesize starch nanoparticles from corn starch using a 20 kHz sonicator with a power of 400 W coupled with a horn with a tip diameter of 13 mm. The corn starch starch granules were suspended in a water-isopropanol solution, and the beaker was kept in a jacketed glass thermostatically controlled by a circulating water system at 10 °C during sonication to obtain the corn starch nanoparticle [30].

3.1.4 Applications of starch nanocrystals

Nanotechnology has the potential to revolutionise the food packaging sector by providing materials with stronger tensile strength, higher moisture barrier, and more effective antibacterial properties [37]. In the packaging of the food industry, research and development are increasing with different ranges of films and nanocoating for various food products. The use of nanoparticles such as starch nanocrystals may change the development of packaging materials of food products with enhanced shelf life [38]. Starch nanocrystals can be utilized as catalysts for antioxidants, flavors, enzymes, and possess antimicrobial properties and anti-browning agents; these characteristics will help to extend shelf life [39]. The packaging of different foods has been made possible with starch nanocrystals due to their higher barrier properties, such as water vapor permeability and oxygen transfer rate. The water transmission rate is reduced by using starch nanocrystals from different botanical origins. Sorbitol-pullulan packaging films decrease the water vapor permeability and increase mechanical characteristics by adding 30–40% starch nanocrystals [40] and adding maize starch nanocrystals to amaranth protein. The chemical and physical characteristics of pea starch films were induced by the addition of potato starch nanocrystals at different concentrations. Therefore, films incorporating starch nanocrystals had a maximum tensile strength and a lower water vapor permeability [41]. Cooked starch is used in paper making as an additive, but the starch paste viscosity increases upon cooking. The use of starch nanocrystals can reduce the viscosity compared to their natural starches and improve the overall performance of paper. The enzymatic browning and physicochemical properties of

different fruits, e.g., apple, are decreased by starch-based nanocomposites [42]. Starch nanocrystals derived from cassava have been used with cinnamon oil and sodium bentonite nanoclay for the packaging of meatballs, and it was observed that microbial growth was reduced. Interestingly, starch nanocrystals incorporated with essential oils showed higher antioxidant activity than commercial plastic packaging materials. [43]

3.1.5 The effect of nanocrystals on barrier properties

Researchers have observed positive and satisfactory effects of utilizing starch nanocrystals as polymeric fillers. Nanocrystals have dimensions lower than 100 nm, which results in better distribution and compactness of the structure of polymers. Both mechanical and barrier properties (water and gas permeability) are improved by incorporating starch nanocrystals. Water vapor permeability is reduced due to the compactness between polymeric structures, leading to water vapor diffusion. It was observed that both the water vapor permeability and water vapor transmission rate of starch nanocrystals were reduced significantly compared to those of normal pea starch. With the addition of 5% starch nanocrystals, the water vapor permeability was lowest, indicating enhanced barrier properties. A decrease in the oxygen transmission rate was observed in polylactic acid nanocomposites with starch nanocrystals as filler, preventing food degradation and spoilage inside the package [44]. Starch nanocrystals derived from waxy maize with 99% amylopectin have been proven to be a tremendous barrier to oxygen [45]. Starch nanocrystals from corn decrease water vapor permeability by 50%, which may be due to interactions between hydrogen and covalent bonds among starch and polyphenolic compounds. These compounds and interactions inhibit the availability of hydrogen groups required to form hydrophilic bonds, therefore reducing the affinity of packaging films towards the water. The oxygen permeability of starch nanocrystals derived from corn starch was recorded as 12.11 $cm^3\mu m\ m^{-2}d^{-1}\ kPa^{-1}$, which indicates a good oxygen barrier. These values were increased compared to the study conducted by [46], who revealed a value of 4.34 $cm^3\mu m\ m^{-2}d^{-1}\ kPa^{-1}$ for nanocrystals derived from the quinoa-starch film. Differences between the starch nanocrystals films may be due to different modes of sample preparations, different types of sources/origins of starch, and differences in water content.

3.1.6 Effect of nanocrystals on mechanical properties

The two most important parameters that define mechanical characteristics are tensile strength (TS) and elongation at break (EB); both play a significant role in indicating the strength of films and their flexibility. The addition of starch nanocrystals induced tensile strength and Young's modulus compared to polylactic acid nanocomposites [47]. The highest tensile strength increased by 3%, which was attributed to the improved interfacial adhesion between the starch nanocrystals and polymer matrix [48]. Lipid addition to rich starch nanocrystals increased the tensile strength while adding some oils, such as oleic acid, decreased the tensile strength when added at a ratio of 1:1. Interactions between the molecules can improve structural bonds among the polymer network. The addition of 5% starch nanocrystals increased, and the highest tensile strength of 9.96 Mpa, while elongation at break values was reduced to the minimum, i.e., 12.58%. Improved mechanical properties may be attributed to the stiffness and dense structure of starch nanocrystals. The tensile strength is reduced when starch nanocrystals are added at 7–9%, while the elongation at break values increases due to a large number of hydroxyl groups on the surface of the starch nanocrystals, which leads to separation of the microphage [49]. The mechanical properties of various Starch-based biodegradable films are presented in Table 2.

Table 2 Mechanical properties of various starch and starch nanoparticle based biodegradable film

Type of starch nanocrystal	Composition of films	Tensile strength (MPa)	%age elongation	Young's Modulus	Citation
Corn	Starch-based biodegradable film	14.22	5.26	13.47	[50]
Wheat	Wheat gluten films	14.05	6.08	14.2	[51]
Potato	Polymeric pouches of different gas barrier properties	14.57	70	14.44	[52]
Pea	Starch nanocrystals-reinforced pea starch films	6.68	26.7	27.56	[53]
Maize	Thermoplastic starch and polysaccharide nanocrystals nanocomposites	1.49	51	14.2	[54]
Rice	Composite films based on rice flour and cellulose fibers	1.80	49	9.6	[55]
Tapioca	Tapioca starch based biodegradable polymer film	0.78	137	0.8	[56]

3.2 Chitin nanoparticles

Chitin is known as poly(b-(1–4)-N-acetyl-ᴅ-glucosamine), and it is a natural polysaccharide first discovered in 1884. It is the second most common biopolymer after cellulose Nature produces chitin as ordered crystalline microfibrils, found mainly in arthropod exoskeletons and fungi and yeast wall cells [57]. It is composed of extended long-chain N-acetylglucosamine polymer-modified glucose [58]. Chitin nanocrystals (ChiNCs can be used as reinforcing nano-fillers for biomedical polymers. Chitin has the ability to transform into individual nanocrystals by downsizing since arthropod shells have hierarchical structures. Acid hydrolysis and TEMPO-mediated oxidation are some methods used to make chitin nanocrystals [59].

3.2.1 Acid hydrolysis

The chitin powder was hydrolyzed in acid at 60°Cand vigorously stirred for 90 min. We collected the residue by centrifugation and repeated the process two more times. A centrifuge was used to centrifuge the reaction mixture at 6000 rpm for 20 min, followed by multiple washes until turbidity was achieved. In the next step, we re-emulsified the precipitate using a homogenizer at 1000 for 10 min and then used ultrasonication for 5 min to disperse it in distilled water [60]

3.2.2 TEMPO-mediated oxidation

A new technique for oxidizing cellulose using TEMPO was recently discovered. Nanochitin can be rapidly prepared by using the TEMPO/NaBr/NaClO system in less than 2 h with C6-carboxylate groups of 0.40*0.60 mmol/g. Chitin powder was disseminated in distal water (Ye et al., 2019). TEMPO and sodium bromide (NaBr2) were added to the dispersion. The oxidation of chitin by TEMPO is initiated by the addition of NaClO solution. The pH of the dispersion was adjusted to 10 at room temperature by the addition of 0.5 M NaOH continuously. The reaction was stopped after the NaOH was no longer utilized by introducing a small amount of ethanol.The suspension could be collected by decanting after centrifuging at 10,000 rpm for 30 min. The suspension was rinsed five times with ethanol after centrifugation [59, 61].

3.3 Chitosan nanoparticle

Chitosan is a polysaccharide derived from the chitin present in the cell wall of fungi and is deacetylated as a primary component. Chitosan is a cationic polymer consisting of (1–4)-2 amino-2-deoxy deoxy-β-ᴅ-glucan and has gained more attention because of its pH sensitivity, biocompatibility, and bioactive properties functions [62]. Chitosan nanoparticles were first defined by Ohya in 1994. He suggested intravenous fluorouracil delivery carried by nanoparticles prepared by emulsification and cross-linking [63]. In food applications, modified chitosan nanocrystals have provided the most emerging applications.

3.3.1 Emulsification and crosslinking

A chitosan nanoparticle was first developed by coupling amino groups of the chitosan molecules with aldehydic groups of cross-linking. In the cross-linking process, the cross-linking oil phase is used as a suspension that, depending on its physical properties, can vastly affect the morphology of the droplets, uniformity, and stability of the W/O emulsion [64]. The preparation of chitosan nanocrystals involves water in the oil emulsion followed by the addition of a cross-linking agent that hardens the formed droplets [63]. Water in oil is prepared by first emulsifying an aqueous chitosan solution in the oil phase and then stabilizing the droplet by using a surfactant, e.g., span 80. Afterward, the stable emulsion was cross-linked with glutaraldehyde, the most versatile cross-linking agent. As a result, a covalent crosslinking reaction takes place between the amino group of chitosan and the aldehydic group of glutaraldehyde and precipitates into the particle. Separation and obtaining fine nanoparticles from emulsions can be achieved via centrifugation, multiple washing steps and vacuum or freeze-drying [62, 65].

3.3.2 Ionic gelation

There are a number of methods available for preparing chitosan nanoparticles, but the ionic gelation technique has attracted considerable interest in nanoparticles, including [66]. Researchers have investigated chitosan nanoparticles since the 1990s, with ionic gelation being one of the most widely used methods for the preparation, described first by [67]. It depends on the ionic crosslinking between charges, the positively charged primary amino group of chitosan, and the negatively charged polyanion, e.g., sodium tripolyphosphate (TPP), as a cross-linking agent because of its nontoxicity and multivalent properties. In this process, a chitosan solution was formed by dissolving chitosan in acetic acid, and then the solution was stirred overnight in a magnetic stirrer at room temperature. Then, aqueous solutions of chitosan and TPP were mixed together under sonication at room temperature in a dropwise manner. After mixing, the pH of the suspension to 7 was adjusted using sodium hydroxide. Through centrifugation at 1200 rpm, the formed particles were separated and washed with water three times. For characterization, nanoparticles were freeze-dried and stored at 4° in a dark atmosphere [68].

3.3.3 Reverse micellization

The first reports of chitosan nanoparticles made from reverse micelles were published by [69]. A reverse micelle is a droplet of water in oil stabilized by a surfactant, e.g., sodium 2 bis (2-ethylhexyl) sulfosuccinate cetyltrimethylammonium bromide used as a surfactant and called Na (AOT). In the method of reverse micellization, a lipophilic surfactant is dissolved in a suitable organic solvent, such as n-hexane, to prepare a W/O microemulsion. In another step, the aqueous phase containing chitosan, the drug, and glutaraldehyde is brought over the organic phase at constant stirring, and reverse micelles take place at this step. Further nanoparticles were separated by evaporation using a rotary evaporator [63, 70].

3.4 Alginate nanoparticles

Alginate is obtained from the cell wall of brown algae, is a natural polysaccharide, and easily gelates with Ca + . A wide variety of bio-applications rely on particle forms, including drug delivery systems [71, 72], food processing [73], enzyme immobilization, and biosensor engineering techniques [74]. A comprehensive review has been conducted on alginate's physical and chemical properties and its use in the production of particles and bulk gels [75]. It is biodegradable, cost-effective, mucoadhesive, biocompatible, and nanoimmunogenic It can even be produced in large quantities at inexpensive prices [76]. Two methods are used to prepare alginate nanoparticles: the complexation method and the w/o emulsification method. Systems ranging in size from 10 to 1000 nm are referred to as nanoaggregates, nanocapsules, and nanospheres.

3.4.1 Complexation method

The formation of alginate nanoparticles can occur via polyelectrolyte complexation in mild aqueous environments unaffected by organic solvents. To make a Ca-alginate pregel solution, a 1:1 (volume ratio) mixture of alginate and calcium chloride solution was prepared. To increase the uniformity of the pregel, calcium chloride (CaCl2) solution was added dropwise to the alginate solution during sonication for 30 s at 120 W. Then different dilutions of the cationic polymer were added, such as poly L-lysine and chitosan, through ionic interactions to form nanoparticles. However, the conventional mixing of Ca-alginate pregels with cationic polymers results in wider particle sizes, and microaggregates are formed, preventing their use as functional particles [12]

3.4.2 Emulsification method

As a part of the emulsification process, alginate is deposited on the interface droplets, and stabilizing methods include chemical and physical intramolecular cross-linking, followed by solvent removal. Alginate nanoparticles were synthesized by emulsification with external gelation. An aqueous solution of alginate mixed with oil containing Span 80 was homogenized to achieve emulsification and sonicated for 10 min. A solution of calcium chloride (with or without chitosan) was gradually added to the emulsion to stabilize the nanoparticles. It was observed that the combination of calcium chloride

and chitosan results in significantly larger nanoparticles than nanoparticles without chitosan [77, 78]. A number of factors affect the size and loading capacity of nanoparticles, including the type of oil phase, order of addition of chitosan and calcium chloride, the addition of surfactant, and the amount of mixing energy during fabrication [79]

4 Techno economic challenges in polysaccharide-based bionanocomposite films

There are numerous challenges and hurdles associated with the various phases of the development of nanoparticles. To achieve a consistent product with the intended physicochemical characteristics and biological behaviors, nanoparticles must be designed and engineered with care, have detailed orthogonal analytical methods, and be scaled up proportionally. The disadvantages of nanocomposite formulation include increased viscosity, dispersion difficulties, optical challenges, and increased sedimentation rate. The properties of polysaccharide-based nanocomposite films are determined by the kind of nanoparticle, the degree of dispersion, and the concentration of nanoparticles in a polymer matrix. The miscibility and compatibility of nanoparticles in the biopolymer solution are critical for achieving the appropriate characteristics for food packaging applications. A relatively emerging concern relating to the safety of food packaging materials is connected to nanosized material, which may inflow into the food items when contact duration is increased. Storage temperature also greatly influenced the infusion of nanoparticles into the food product. The health risk associated with nanocomposite films depends on the rate of migration of nanomaterials from outer packaging into food and the toxicity of the nanomaterials employed. Migration testing, cytotoxicity testing, and eco-toxicity testing are required to determine the environmental implications of nanomaterials used in food packaging prior to extensive use of these materials. In addition to these, more investigations are needed to solve issues relating to mechanical, thermal, moisture and gas barrier properties of the polysaccharide-based nanocomposite films for food packaging applications.

5 Conclusions

Packaging materials such as petroleum-based plastics are responsible for the maximum portion of environmental waste and can be replaced by biodegradable nanomaterials such as starch, chitin, alginate, and chitosan. These biodegradable nanomaterial based packaging materials must be safe in addition to safeguarding the food from dirt or dust, air, light, moisture, and pathogenic germs. Under its intended circumstances of usage, the packaging should be inert, inexpensive to create, lightweight, and capable of withstanding harsh conditions during processing or filling. These food packaging has to be be resistant to a variety of storage temperature and relative humidity of environment. The different studies showed that incorporating nanomaterials in biodegradable polymers can enhance the gas and water vapour barrier functions and improve mechanical properties. Migration and permeability to ambient gases, water vapour, or natural compounds contained inside the food being packed is a major concern in food packaging. Thus, further studies are required to optimise the migration and permeability to ambient gases, water vapour, or natural substances through the packaging material, as well as to determine the toxicity of nanomaterials that may be incorporated into food items.

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