Chapter 5
Starch-Based Nanostructured Materials in Edible Food Packaging

Tabli Ghosh, Munmi Das, and Vimal Katiyar

5.1 Introduction

From early days, starch and its derivatives are a potential candidate in various food industries including beverages, food packaging, confectionary, bakery products, instant meals, and others. In food packaging industry, the increasing environmental concerns related to the consumption of plastics based on petroleum resources have led to the development of healthier products prepared with sustainable and environment-friendly materials [1, 2]. The eco-efficient products are expected to meet with the ecological, environmental and economic requirements, and thus, focus has been emphasized on the production of edible films, using starch-based materials for existing noteworthy property [3]. The conventional plastics used in food packaging are generally contaminated by food matter, and thus, their recycling becomes impractical. Thus, fabrication of edible food packaging using starch nanostructured materials with tailored properties using novel strategies can resolve the problems related to recycling and waste generation. Considerably, starch-based nanostructured materials provide a new platform in the development of novel edible packaging systems [4]. Considerably, the development of sustainable packaging has become the foremost requirement using naturally available materials as a replacement due to the environmental concern [5]. Starch, a promising natural polysaccharide, is used as an efficient and sustainable edible packaging material because of its abundancy, renewability, low cost, biodegradability, and thermosplasticity compared to other natural resources.

T. Ghosh · M. Das · V. Katiyar (✉)
grid.417972.eDepartment of Chemical Engineering, Indian Institute of Technology
Guwahati, North Guwahati 781039, Assam, India
e-mail: vkatiyar@iitg.ac.in

T. Ghosh
e-mail: tabli@iitg.ac.in

V. Katiyar and T. Ghosh, *Nanotechnology in Edible Food Packaging*,
Materials Horizons: From Nature to Nanomaterials,
https://doi.org/10.1007/978-981-33-6169-0_5

Moreover, the use of starch-based packaging materials is growing day by day due to water solubility and easy biodegradation. The various sources of starches are cereals (rice, wheat, maize), root vegetables (potatoes and cassava), stems, pith (sago), and others. The various categories of starches are obtained based on sources, and amylose and amylopectin content (waxy starch, normal starch, high amylose starch), and others. Among the available sources, cassava starch is extensively used category of starch due to the low cost, colorless, good oxygen barrier, and other features. The rich sources of starch-based foods are fast food, French bread, brown rice, potatoes, whole wheat pasta, sweet corn, bananas, apple pie, etc. Based on this discussion, starch is safe for consumption, thus targeted to be used as an edible food packaging material. However, the commercialization of starch films is restricted due to poor mechanical property, moisture sensitivity, and others. In the presence of dense interchained H-bonds network, starch films exhibit brittleness which thereby lead to cracking. To increase the elasticity and mechanical property of these films, plasticizers or blending agents are incorporated into the polymeric network, consequently increasing the molecular movement, which further decreases the glass transition temperature (T_g). However, safety measures should be followed to ensure the developed edible packaging to be non-toxic in nature [6–8].

The present-day demand to produce novel materials with improved shelf life and quality has led researchers to a new dimension in the food packaging industry using nanotechnology [9]. Nanostructured materials have at least one of its dimensions in nanometer range and are usually classified as polymeric nanoparticles (NPs), liposomes, nano and microemulsions in the food technology and also exist as layered films, or in cluster forms [10]. These nanostructured materials contribute as functional materials by improving the mechanical strength, barrier property, antimicrobial and antioxidant activity which in turn increase the quality and shelf-life of the food [11]. In this chapter, a discussion on the preparation and property analysis of starch-based nanostructured materials will be discussed with appropriateness of their applications as a noteworthy candidate for edible food packaging. Moreover, the effect of starch-based nanostructured materials with other added agents will also be discussed. In this regard, the improved packaging features of starch nanomaterials can be modified using plasticizers, cross-linkers, biopolymers, and others.

5.2 Effectiveness and Categories of Starch-Based Resources

5.2.1 Components of Starch

Starch is used as a versatile material in the food industry in the form of gelling component, stabilizer, thickener, water retainer, which enhances the texture, adhesiveness, gel formation, moisture retention, miscibility between various components, and viscosity of the end products [11]. The basic structure of starch is $(C_6H_{10}O_5)_n$, and it mainly comprises two biomacromolecules amylose and amylopectin, along with the presence of a small amount of protein, lipid and phosphorus. The dimension of starch granules is within the range of 2–100 μm consisting of crystalline and amorphous lamellae. Amylose is a linear glucose molecule with few branches connected by (1–4) α-D-glycoside bonds and comprises around 20% of normal starch, whereas amylopectin consists of highly branched α-D-(1–4) glucopyranose units interconnected by 5% α-D-(1–6) glycosidic linkages [12]. Depending on the ratio of amylose/amylopectin content, starch is again classified as waxy, normal, and high amylose starch where waxy starch comprises a higher amount (90% or more) of amylopectin and relatively less amylose. Similarly, normal starch constitutes around 15–30% amylose, and high amylose starch contains an amylose content of more than 50% as shown in Fig. 5.1. The amylose and amylopectin molecules are present in an alternating interwined manner in the starch granule [11, 13, 14]. Starch is usually insoluble in water at room temperature but when heated swells and disintegrates. Further, the water solubility property of starch depends on the composition of amylose and amylopectin. The swelling phenomenon of starch takes place by the formation of H-bond between the water molecules and free hydroxyl group of the glucan chains at a granular level [15].

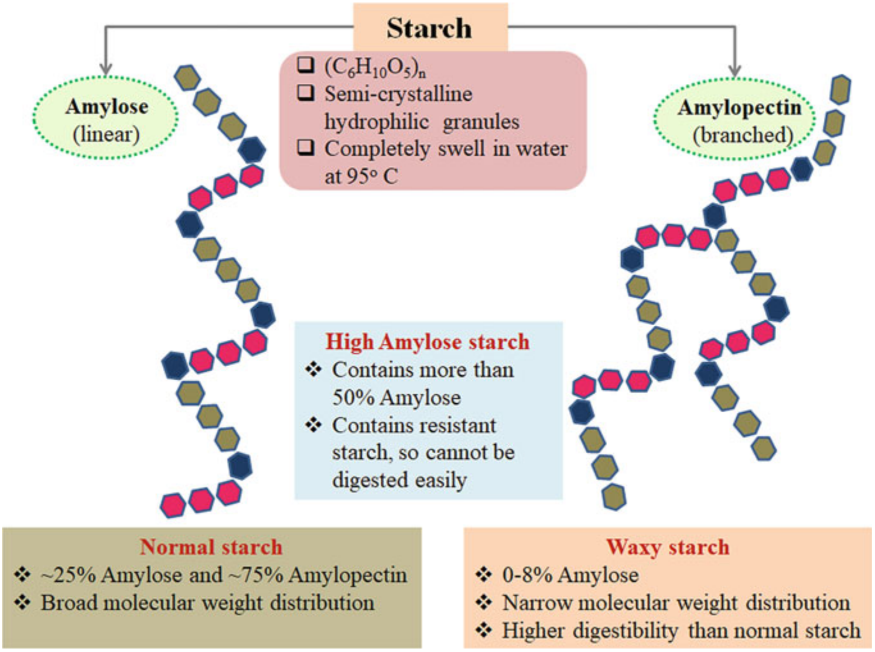

Fig. 5.1 Classification of starch, based on amylose and amylopectin content

5.2.2 *Sources of Starch*

Starch is extracted mainly from plant sources as an energy reserve, specifically from seeds, roots and stems, crop seeds, tubers, and also from some fruits. Some common examples of starch-based sources are rice, wheat, potato, corn, maize, cassava, apple, tomato [12, 16]. Table 5.1 illustrates some common types of starch based on their botanic origin, size, and amylose content [12, 17]. The amylose content varies from 0.5 to 83% based on their botanical origin, which further, influence the rheological, thermal, processing characteristics of starch as well as their structural features. As mentioned in earlier section, the ratio of amylose/amylopectin also determines the mechanical strength, swelling behavior, oxygen permeability, gelatinization, viscosity, water binding capacity, and texture of the starch-based materials. These properties are source-dependent and an increase in amylose content increases the thermal stability of starch-based materials [18]. Additionally, resistant starch, another type of health beneficial starch, is obtained from beans, legumes, lentils, peas, whole grains (oats, barley), cashews, green bananas, cooled rice, cooked rice, raw potato starch, hi-maize flour, etc. The beneficial features of resistant starches are increase stool weight, reduce secondary bile acids, stimulate immune system, reduce intestinal pathogen levels, reduce risk factors relating large bowel cancer, etc.

5.3 Starch for Targeted Food System and Edible Food Packaging

From very early days, food preservation maintains the nutritional level and quality of foods intact, by increasing the shelf life of the packaged edible food. Food preservation technique is a complete cycle starting from growing the food to distribution of the food to the end users. Food preservation protects the food product by improving its shelf life, antimicrobial activity resulting in a sustainable edible packaging. Commonly used food preservation processing techniques are drying, freezing, chemical preservation, chilling, pasteurization, fermentation as shown in Fig. 5.2 [19, 20].

Starch-based materials are also used for developing food products and packaging materials to improve the shelf life of food products and others. The intake of corn starch has many health benefits such as reduce blood pressure, boost immune system, source of vitamins and minerals, and antioxidants. The starch-based derivatives and nanostructured materials have various noteworthy applications including (1) Food packaging sector as matrix and filler materials in edible and non-edible packaging for improved product life; (2) Pharmaceutical industry: Starch is used for developing colloidal formulations; (3) Food Products: Sauces, bread, candies, baby foods, sausage, thickeners, and others. The main functions of starch in food products are thickener (puddings, sauces, pie fillings), binder (breaded items, formed meats),

Table 5.1 Properties of different starch, based on their botanic origin

Source	Maize	Barley	Wheat	Rice	Waxy starch	Waxy barley	Arrowroot	High amylose	Cassava	Sweet potato	Potato	Smooth pea	Wrinkled pea	Ginger
Average granule size (µm)	30	8–26	30	2–7	15	8–26	>30	5–25	3–30	3–27	40–100	2–40	17–30	>20
Apparent amylose content (%)	25–28	29.8	21.5–26.6	29.1	0.5	9.1	20.8	60–73	19.8	22.6	26.9	33–48	60–80	26.5

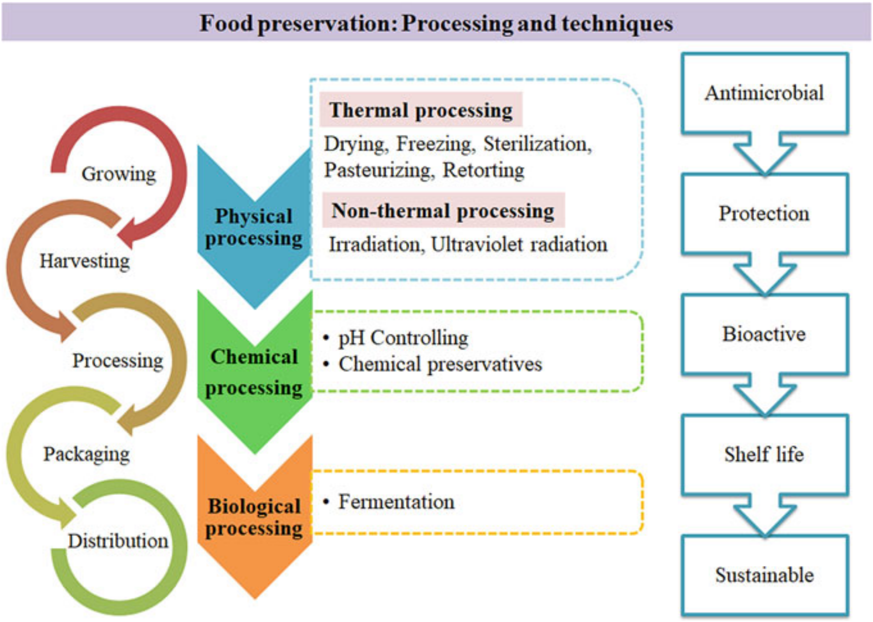

Fig. 5.2 Food preservation techniques in edible packaging

coating (toppings, candies, glazes), water binder (cakes, jellies), releasing agents (candy making), texture modifier (meat products, processed cheese), fat replacer (dairy products, baked goods, salad dressings), etc. Additionally, the functions of starches in food products are adhesion, thickening agents, shaping, molding (gum drops), gelling, glazing, binding, and others. The various forms of starch to be used in food systems are nanostructured materials (NPs, nanowhiskers, nanocrystals (NCs), etc.), nanofilms, hydrogel, microbeads, microsphere, tablets, thermoplastic foam, and others.

5.4 Global Industrial Starch Market Based on Region, Source, Application and Industry

The global industrial application of starch-based resources is food industry, chemical industry, beer industry, modified starch industry, biopolymers, medicine, animal, and others. Besides, the main sectors of starch-based non-food industrial applications are adhesives, paper industry, construction industry, cosmetics, metals industry, textiles, mining, etc. Interestingly, food preservation holds a crucial position in the global economy, and it is predicted that the industrial starch market will grow from USD 72.51 billion (2016) to 106.64 billion USD by 2022.

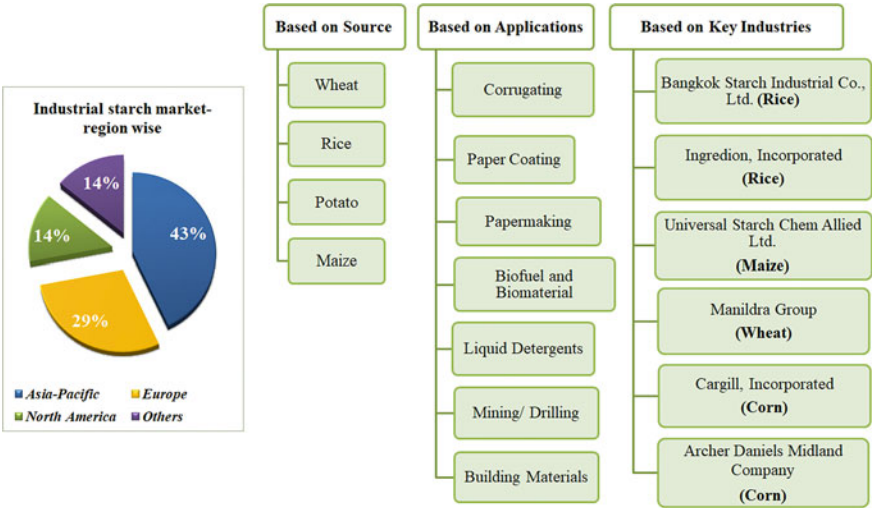

Fig. 5.3 Global industrial starch market based on region, source, application, and industry

Figure 5.3 elaborates the division of the industrial starch market globally among North America, Asia-Pacific, Europe, and other parts of the world. China alone contributes to half of the global starch consumption resulting in the emerging Asia-Pacific market with a wide range of applications. The industrial starch market is classified according to the type of native starch and their derivatives and sweeteners [21]. Figure 5.3 showcases various industrial starch manufacturers across the globe, which includes Cargill (USA), Archer Daniels Midland Company (USA), Universal Starch Chem Allied Ltd. (India), Ingredion Incorporated (USA), Manildra Group (Australia) and Bangkok Starch Industrial Co., Ltd. (Thailand) and their specialized applications as biofuel and biomaterial, mining and building materials as well as pharmaceutical, corrugating, and paper-making materials [22].

5.5 Extraction of Starch from Available Sources

The pure starch extracted from plants appears as a white-colored powdery material in the form of distinct semi-crystalline granules within 1–100 µm size range, insoluble in cold water and alcohol and is particularly used as a thickener or binding agent in paper and food industry [12, 16]. Commonly used extraction methods are alkaline extraction, aqueous extraction, ethanol extraction, ultrasound extraction, microblending and homogenization. The starch structure and morphology vary with every extraction process. The extraction methods of various starch based on their botanic origin are mentioned in Table 5.2. The starch extraction has been reported from available sources such as rice beans, white garland lily rhizomes, pigmented rice, *pachyrhizus ahipa* roots, radix puerariae, plantain (*Musa paradisiaca*) peel,

Table 5.2 Extraction of starch using various methods from different sources

Si. No.	Source	Pretreatment methods	Extraction methods	Starch granule size/yield%	Reference
1.	Rice beans	Milling and sieving followed by hydrothermal processing	a. Aqueous extraction b. Ethanolic extraction	a. 15–25 µm b. 25–35 µm	[23]
2.	White garland lily rhizomes	Peeled and cut	Aqueous extraction	Thickness = 2–6 µm Length = 12–38 µm	[24]
3.	Pigmented rice (white, red, and black)	–	Aqueous extraction	White rice = 44.0%, Red rice = 47.0% and Black rice = 35.7%	[25]
4.	*Pachyrhizus ahipa* roots	Roots are washed with water and immersed in NaClO solution to sanitize for 10 min, peeled and cut	Aqueous extraction	Starch yield = 15.7%	[26]
5.	Radix Puerariae	Peeled, cut, and grinded	High-intensity ultrasound	High amylose starch yield of 44.5%	[27]
6.	Plantain (*Musa paradisiaca*) peel	Washed and sanitized with NaClO and cut	Aqueous extraction	Yield = 16.6–48.5%	[28]
7.	Sorghum	Washed and dried to remove impurities, followed by milling	Homogenization	Yield = 26%	[29]

sorghum and others [23–29]. The pretreated rice beans (pretreated method: milling and sieving followed by hydrothermal processing) are reported to develop starch granules using aqueous and ethanolic method having granules size of 15–25 and 25–35 µm, respectively [23]. Additionally, starch granules having thickness and length of 2–6 and 12–38 µm, respectively, can be extracted from white garland lily rhizomes using aqueous extraction approach [24]. The yield of starch varies based on the available source and starch extraction methods. In this regard, the yield of starch extracted from white rice, red rice, and black rice using aqueous extraction is 44.0, 47.0 and 35.7%, respectively [25]. On the otherhand, the extraction of starch from *pachyrhizus ahipa* roots using aqueous extraction method can provide starch yield of 15.7% [26]. The peeled, cut and grinded radix puerariae is used to extract

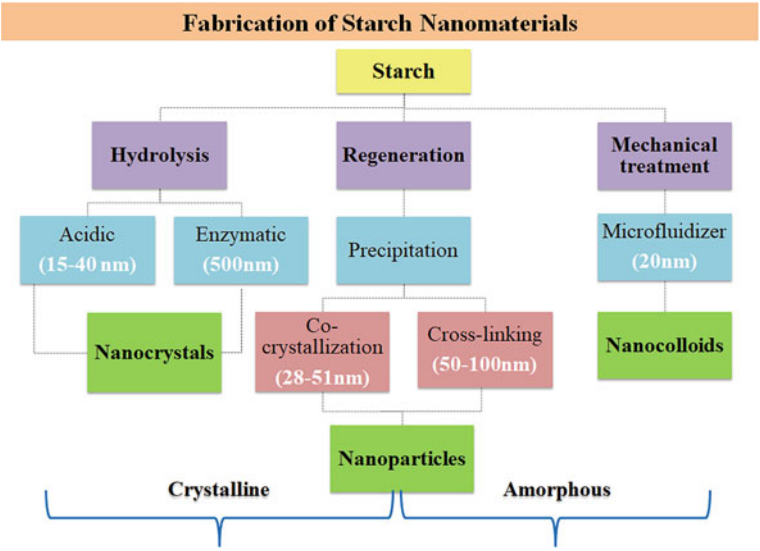

Fig. 5.4 Fabrication methods to obtain starch nanomaterials

high amylose starch (yield of 44.5%) using high-intensity ultrasound [27]. Additionally, using the aqueous extraction method, starch with a yield of 16.6–48.5% can be extracted from plantain (*Musa paradisiaca*) peels [28]. The several extraction methods of starch are aqueous extraction, ethanol extraction, ultrasound extraction and homogenization.

5.6 Fabrication of Starch Nanomaterials

Starch nanomaterials are categorized into different forms, such as starch NPs, NCs, and nanocolloids based on their size, shape, crystalline behavior, and preparation method. Various methods including chemical, physical, enzymatic, and blending are used to fabricate starch nanomaterials from the native starch granules. The commonly used methods in the fabrication of starch nanomaterials are discussed below and shown in Fig. 5.4.

5.6.1 Starch Nanocrystals: Acid Hydrolysis and Enzymatic Hydrolysis

Pure starch granules are semi-crystalline in nature with an onion-like structure in which the amylose content constitutes the amorphous region, and amylopectin content contributes to the crystalline region. Upon hydrolysis, the amorphous content is discarded to give NCs with higher crystallinity. Starch NCs (STNCs) contribute in increasing the mechanical properties when combined with a polymer matrix and are dominantly used as emulsion stabilizers, in bioplastic packaging and as drug carriers [30, 31].

Acid hydrolysis. Starches with higher amylopectin content, for example, waxy maize starch is mostly used for the preparation of NCs due to its higher degree of crystallinity. The extracted pure starch material usually undergoes a pretreatment prior to hydrolysis, where moisture content of starch is adjusted by the addition of distilled water, aqueous alcohol or alkaline solution. Further, these starch suspensions are washed, centrifuged, neutralized followed by drying of the precipitated starch. The obtained starch powder is then grinded and filtered through a sieve [31, 32]. In a recent study, STNCs from Quinoa starch were obtained by dispersing the starch powder in a sulfuric acid solution, followed by incubation for 5 days with continuous stirring at 200 rpm at a fixed temperature. The hydrolysis continued for 5 days, and then, the starch solution was centrifuged, neutralized to obtain a suspension which was further homogenized and freeze-dried to give STNCs of 22.8 and 6.8% yield, respectively, at 35 and 40 °C. The characteristics and yield percentage of STNCs vary depending on the starch source and hydrolysis conditions, such as acid type and concentration, reaction temperature and time [33].

Enzymatic hydrolysis. The optimum longer duration (5 days) of acid hydrolysis to obtain STNCs led to the utilization of enzymes in order to lessen the hydrolysis time and keep the inherited characteristics of STNCs intact. The starch modifying enzymes, for example, α-amylase, amyloglucosidase, aspergillopepsin1, and glucoamylase are generally used to improve the qualities of starch in enzymatic treatment [30]. Starch converting enzymes are usually classified as amylases and transferases, where former hydrolyzes the glycosidic bonds and the latter helps in transfer of the bonds. Enzymatic hydrolysis, with the use of amylases, helps in modifying the viscosity and degree of polymerization of starch. In a study, α-amylase enzyme enabled the fragmentation of starch granules in just 3–6 h leading to the formation of crystalline STNCs [34, 35]. In a study, waxy rice starch was hydrolyzed enzymatically for 3 h using α-amylase, followed by ultrasonication in ethanol to obtain 500 nm-sized STNCs [36]. In a typical enzymatic hydrolysis pretreatment, initially the enzyme is dissolved in a pH buffer (pH = 5.5–6.9) solution. To this enzyme solution, a weighed quantity of starch powder is added and allowed to incubate at 37 °C for a day. Further, the enzyme activity is stopped with the addition of ethanol, and the obtained hydrolyzed product is centrifuged and washed and dried overnight at 35 °C to give STNCs [35, 36].

5.6.2 Starch Nanoparticles: Regeneration and Cross-linking

Regeneration. The formation of amorphous starch NPs by precipitating the gelatinized starch in a chosen solvent usually refers to the regeneration process.

Development of starch NPs for utilization in nanocomposites preparation has grabbed attention due to its unique and improved mechanical and barrier properties. The most recently explored processes to develop starch NPs efficiently are (a) precipitation of gelatinized amorphous starch, (b) combination of enzymatic hydrolysis and complex formation, and (c) reactive extrusion or microfluidization [37].
Ma et al. reported the synthesis of starch NPs by preparing a gelatinized starch solution and further precipitating this solution in ethanol [38]. However, this process is not considered economical as it involves the use of a large quantity of solvent for precipitation and difficulty in controlling the proper size of NPs. To reduce the consumption of solvent, Hebeish and coworkers used aqueous alkaline (NaOH) solution as the solvent system to disperse the maize starch. This starch suspension was then stirred continuously at 25 °C for 120 min to obtain a uniform gelatinized starch. Absolute ethanol was then added as a precipitating agent in a dropwise manner to this gel suspension under continuous stirring to obtain spherical starch NPs of 135–155 nm size range [39].

Cross-linking. Starch NPs possess reactive surface which tend to agglomerate, and thus, a chemical modification is required to maximize its dispersion in aqueous medium. Ren et al. modified the surface properties of starch NPs with the use of sodium hexametaphosphate (SHMP) as a cross-linker. The modification was carried out below gelatinization temperature (40 °C) of the waxy maize starch which resulted in a stable and uniform dispersion of starch NPs in water [40]. Also, Ma et al. used citric acid as a cross-linker to stabilize the NPs, and the modified starch exhibited the properties of resistant starch with various health benefits. These citric acid modified starch NPs when incorporated into the polymer matrix resulted in improvement of glass transition temperature, barrier properties, and tensile strength [38].

5.6.3 Starch Nanocolloids: Mechanical Treatment/Microfluidization

Microfluidization enables the preparation of nanocarriers by reducing microsize to nanometer scale without disturbing the crystal structure of the starch granules. The particle-size distribution can also be tuned by adjusting the processing conditions. Some mechanical treatment involves the use of ultrasound waves, which converts to energy by the formation of cavity in the starch microemulsion. This results in the formation of bubbles which collapse and produce more energy thereby reducing the droplet size in the emulsion [41].

A microfluidizer uses high-pressure homogenization process which basically manipulates the steady flow of liquid via microfabricated channels. Various external factors activate the flow of liquid through the channels, such as pressure, mechanical pumps, and micropumps. Microfluidization is carried out without any chemical or physical pretreatment. Thus, the particle size of a high amylose corn starch slurry containing sediment and dispersion in water is reduced from 3 to 6 μm to a nanometer scale of 10–20 nm, under 207 MPa pressure by this technique. This high-pressure homogenization transformed the starch sol into a stable gel-like suspension and increased the viscosity of the starch nanocolloid without affecting its thermal stability [42].

5.7 Features of Starch and Its Derivatives for Potential Application in Food System

As discussed in Fig. 5.5, the features of starch and its derivatives for potential application in food systems are biological properties, thickening property, rheology enhancer, film-forming property, water binding capacity, and others. In this regard, a brief discussion on the various beneficial properties of starches for edible food packaging has been discussed in the below section.

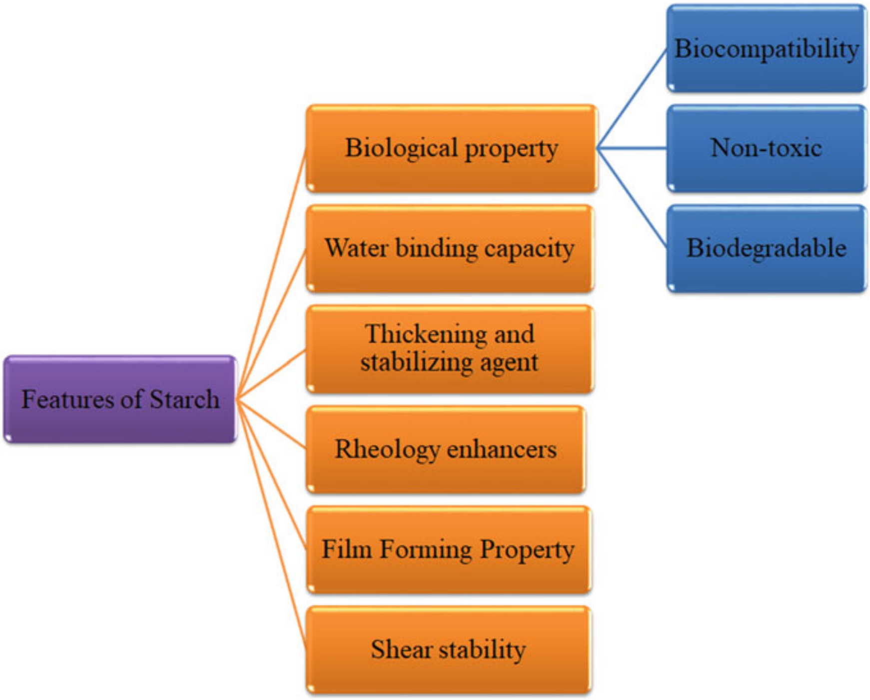

Fig. 5.5 Features of starch for application in food system

5.7.1 Biological Properties: Biocompatible, Non-toxic and Biodegradable

Starch is a biobased material having non-toxic, biocompatible, and biodegradable nature, making it a potential candidate for edible food packaging and others food systems. The starch polymers do not induce toxicity over different cell types and further reported to offer important cell behavior with immune potential [43]. The biocompatibility test of starch-based composite can be done via cell adhesion test and cytotoxicity test, where the starch polymers proved to exhibit cytocompatibility to be used as a biomaterial [44]. Additionally, the biodegradable starch-based materials have potential application in biomedical section as the materials do not provide any adverse effect in in vitro and in vivo models [45]. The biodegradable nature of starch and its derivatives make it a promising candidate to develop sustainable packaging materials in the form of foam, films, hydrogel, coatings, and others. In this regard, improved oral delivery of poorly water-soluble drugs can be obtained using biodegradable porous starch foams [46]. The several biodegradable polymeric materials which are used with starch for focused applications are proteins, cellulose, gums, which help to increase the shelf life of food products when used as a food packaging material [47]. The preparation of bionanocomposites of polymers has some additional benefits to be used in food packaging (edible and non-edible) are (1) Soil composting due to microbial action; (2) Controlled degradation using nanomaterials; (3) Use of renewable resources with improved property; (4) Degradation by water and sunlight; and others.

5.7.2 Water Binding Capacity

The thermo-mechanical properties of starch-based films are influenced by water binding capacity of starch, where the water binding capacity of starch is dependent on the hydrophilic sites, which can be modified through plasticizers and molecular substitution. The water binding capacity of starches can be measured using differential scanning calorimetry (DSC) method or filter paper suction pressure method. The water binding capacity of starch depends on the amylose/amylopectin ratio, which further influenced by the starch type or sources such as high amylose rice, waxy rice, and others. The increase in amylose content of starch reduces the water binding property of starch molecule. Considerably, the pregelatinized starch has a disruptive internal structure of granules which increase the water binding capacity of starch. However, the chemical modification of starch has an ability to block the route to water flow in the granules, which in turn reduce the water uptake ability of starch. Additionally, molar substitution of hydroxylpropyl maize starch also influences the water binding capacity [48]. The water binding capacity of starch can be decreased by developing cross-linked starch with phosphorus oxychloride [49]. The type and concentration of plasticizers effect the hydration property of plasticized starch film [50].

5.7.3 As Thickening and Stabilizing Agents

The foam/emulsions can get stabilized using thickening agents such as starch, gums, and others. The starch and protein systems as foaming and stabilizers are used. Furthermore, starch is used as thickeners and stabilizers in various food products including pudding, soups, gravies, salad dressings, pastas, and others.

5.7.4 Rheology Property

The rheological property of starches is pasting property, viscosity of starch paste, and rheological features of starch gel. The addition of food additives modifies the rheological properties of starch such as lipids, salts, sugars, and others. The rheological behavior of starch is a crucial parameter to control the properties required for food applications. The thermal transition of starch-based films is also influenced by rheological property such as molecular mechanism and enzyme digestibility. Additionally, the rheological property of starch helps to offer carbohydrate concentration, heating rate for developing products, and other processing condition.

5.8 Modification of Starch and Nanostarch for Edible Films and Coating

Starch is a second most abundantly available biomass materials in nature, which is available as a source of stored energy. Native starch has many limitations such as limited digestibility, and poor functional properties. In this regard, the different types of modified starches are acid-treated starch, alkaline-treated starch, dextrin, oxidized starch, bleached starch, starch acetate, acetylated oxidized starch, starch sodium octenyl succinate, hydroxypropyl starch, hydroxypropyl distarch glycerol, hydroxypropyl distarch phosphate, enzyme treated starch, and others. The various routes of modifying starch-based films have been represented in Fig. 5.6. The starch has a wide application in the field of packaging materials such as biocomposite films, edible films, coatings, water absorbent polymers, and encapsulation. Thus, starch has gained a considerable attention in attaining a wide usability for versatile applications due to the complete biodegradable nature and provides potential functional and nutritional properties. However, the thermoplastic starch is widely used for developing commercial packaging materials in the form of carry

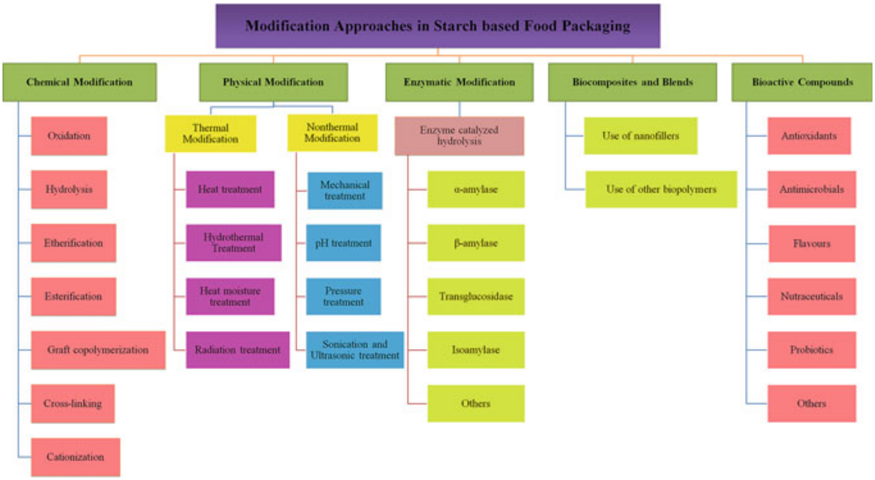

Fig. 5.6 Modification of starch and nanostarch for edible films and coating

bags and foams. Interestingly, thermoplastic starch has some noteworthy properties in comparison with starch such as improved plasticity and thermally processability, where the type of plasticizers in developing thermoplastic starch effects the mechanical property, glass transition temperature of the materials, and the use of glycerol provides less rigidity. The functional property of starch can be tailored-made by varying the dimensions (shape and size) of starch, proportion of amylose and amylopectin, distribution of chain length, etc.

5.8.1 Chemical Modification

The hydrophilicity of starch-based films is a main constraint in limiting its use in the field of edible food packaging. The chemical modification of starch helps to improve the hydrophobicity by substituting the hydrophilic groups of starch molecules. The chemical modification of starch includes the formulation of starch derivatives through functionalization technique such as etherification, esterification, cross-linking, and grafting. The cross-linking agents used in starch modification include glutaraldehyde, boric acid, sodium trimetaphosphate, hydroxypropylation-acetylation, hydroxypropylation-cross-linking, etc. Additionally, the decomposition reaction of starches includes acid hydrolysis, enzymatic hydrolysis and oxidation. The chemical modification approaches help to modify the structure of native starch, which in turn influence the starch film property. The use of plasticizers can improve the properties of starch-based films. In this regard, the several plasticizers for developing edible food packaging include glycerol, sorbitol, formamide, xylitol, etc. The plasticized sago starch using modifying agent such as sorbitol can offer improved thermal features such as improved heat sealability and reduced onset temperatures. The citric acid is used as a modification agent in starch/hydroxypropyl methylcellulose-based films such as reduced glass transition temperature. The use of hydrochloric acid in fabricating acid hydrolyzed starch offers increased heat resistance. Starch nanostructured materials have surface hydroxyl groups and high specific area, which provide the potential to tailor the packaging property via surface chemical modification, providing surface functionality. The modified starch in the form of starch nanocrystal (STNC) has high surface area and thus provides better dispersion property in water than starch granules. Further, the oxidation of starch produces starch oxides, starch radicals; esterification of starch produces starch acetylation; and etherification of starch produces carboxymethylation, hydroxypropylation, and hydroxylethylation.

5.8.2 Physical Modification

Starch modification using physical methods is obtained using thermal and non-thermal methods. The thermal method for starch modification includes heat treatment (simple oven heating, super heating, extrusion, fluidized bed heating), hydrothermal treatment, heat-moisture treatment, and radiation treatment (microwave irradiation, ultraviolet irradiation, gamma irradiation, electromagnetic irradiation). On the otherhand, the mechanical treatment for starch modification includes mechanical method (simple milling/grinding, mechanical activation by stirring), pressure treatment (high-pressure treatment, pressure treatment, osmotic pressure treatment, hydrostatic pressure treatment), ultrasonic treatment (simple, ultrasonication, high-pressure sonication), cold plasma, deep freezing, etc. The physical modification techniques of starch include the use of ultrasound waves, microwave-radiation, osmotic pressure treatment, pulsed electric field, moist-heat treatment, annealing, gamma radiation, dry heating, and others. This approach includes the treatment of starch granules under different pressure, moisture combination, shear, and others. The physical modification of starch using ultrasonic waves provides reduced reaction time, improved degree of substitution, and others. The application of dry heat to starch provides improved water binding capacity; application of gamma irradiation offers improved mechanical and swelling property [51]. The physical modifications of native starch can deliver tailored-made features of water solubility and reduced particle sizes. The physical modification of starch is attained via several approaches such as heat-moisture treatment, annealing (annealed starch), extrusion, freezing, microwave treatment, retrogradation, pregelatinization (obtained by roll-drying, spray, thermal), radio treatment (radio treated starch), and others.

5.8.3 Enzymatic and Genetic Modification of Starch

The enzymatic modification of starch produces various constituents such as maltodextrin, cyclodextrin, and amylose. The enzymatic or genetic modified starch provides novel functionality in starch due to stability and bioavailability. The enzymes for starch modification include α-amylase, β-amylase, transglucosidase, isoamylase, and others.

5.8.4 Biocomposites and Blends of Starch and Its Derivatives

The starch-based composites and blends are developed to provide tailored-made attributes such as chitosan, protein, and cellulose. The attributes of nanostarch such as reaction activity and unique surface area make it a potential nanofiller to develop biocomposites with tunable properties. The nanostructured starch can be obtained as STNCs, starch NPs, and nanocolloids. STNCs can be extracted using acid hydrolysis process such as acidic and enzymatic hydrolysis. The starch NPs can be obtained via regeneration and cross-linking process, whereas nanocolloids can be obtained via mechanical treatment and microfluidizers. The limitations of starch include hydrophilicity, thermal decomposition, and brittle in nature. To combat these limitations, starch and its nanostructured forms are modified via following several routes such as chemical, physical and enzymatic methods. The properties of starch are also improved by making blends with biopolymers. The oxidized starch includes hydroxypropylation, sodium hypochlorite, hydrogen peroxide, persulfate, etc. The oxidized starch is used to coat food products to maintain the food properties. This specific biopolymer has a matrix forming properties to develop biocomposite-based edible food packaging. The fabrication of starch-based biocomposites can be done by dissolving starch at higher temperature followed by mixing of the subsequent biopolymeric solution as shown in Fig. 5.7. As represented in Fig. 5.8, the surface of starch-based biocomposites can be modified using gum arabic and other filler materials as evident by field-emission scanning electron microscopy (FESEM). The tailored-made features of starch biocomposites are obtained by using different types of nanofiller materials such as (1) Polysaccharide-based nanoreinforcements from cellulose, starch, chitosan, chitin, etc.; (2) Protein-based nanoreinforcements; (3) Carbonaceous nanofillers; and (4) Phyllosilicates and others [52].

5.8.5 Addition of Bioactive Compounds

The bioactive starch-based films and coatings can be fabricated with the aid of antimicrobial and antioxidant agents. Additionally, nanosystems of starch are also used in encapsulating different bioactive compounds such as caffeine, curcumin, ciprofloxacin, and others for increased bioavailbility and stability. The inclusion of bioactive such as antimicrobials, antioxidants, probiotics, and flavors to starch

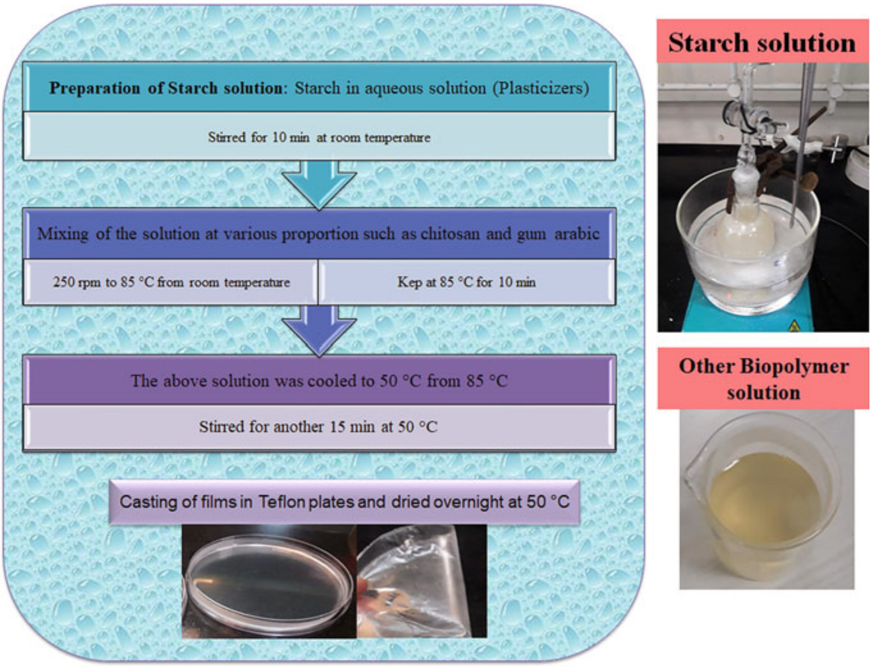

Fig. 5.7 Fabrication of starch-based biocomposites using chitosan and gum arabic

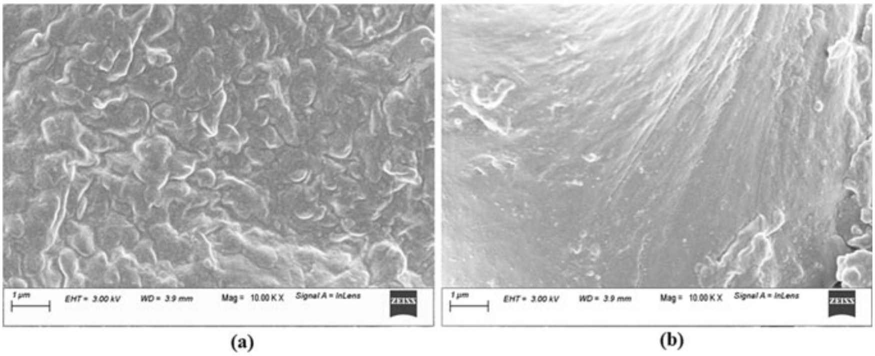

Fig. 5.8 FESEM micrograph of **a** starch/chitosan and **b** starch/chitosan/gum arabic biocomposites

provides improved film properties in terms of functionalized starch-based edible coating assisted by bioactive materials. Additionally, starch is used to encapsulate bioactive compounds. The used bioactive compounds in starch films are antimicrobials, antioxidants, probiotics, nutraceuticals, flavors, and others with a focus to develop functional food products.

5.9 Case Studies on Nanostarch-Based Edible Food Packaging

As mentioned in the earlier section, the acid hydrolysis of starch granules for a long period can hydrolyze the amorphous region, which helps in separating the crystalline part of the starch by fabricating STNCs. However, the acid hydrolysis is generally held at temperature below gelatinization temperature. The STNCs fabricated from waxy maize starch granules via acid hydrolysis (sulfuric acid) can provide relative crystallinity of 63% after 6 days of hydrolysis. The size ranges of STNC fabricated from waxy maize starch granules are 40–80 nm (as evident by transmission electron microscopy (TEM)). The nanocomposite films based on STNCs and carboxymethyl chitosan can provide maximum tensile strength of 29 MPa; and further, the water absorption and water vapor permeability can also be improved using STNC; whereas, the percentage elongation at break decreases with increased STNCs [53]. The STNCs from potato starch granules (fabricated using sulfuric acid-based hydrolysis) and sour lemon peel extract can be used to prepare edible coating on chicken fillets [54]. The application of the edible coating on chicken fillets improves the physicochemical, texture, and sensory properties during 12 days of cold storage. Additionally, high antioxidant ability (against oxidative deterioration) and antimicrobial property (against microbial spoilage) in chicken fillets can be obtained using coating solution of STNC (4.0%) and sour lemon peel extract (5.62%) prepared at 51.17 °C for 43.29 min. The STNC can be fabricated from waxy maize starch via acid hydrolysis at 35 °C, and the fabrication of STNC-reinforced sorbitol plasticized pullulan-based edible films can deliver improved packaging properties in terms of crystallinity, water uptake behavior, mechanical properties, and others [55]. The nanocomposite films based on STNCs and cross-linked cassava starch can be used as an edible coating for Huangguan pears, where the nanocomposite films can maintain texture, color, soluble solids, cell membrane permeability, and other properties of pears [56]. The films based on cross-linked cassava starch with 6% STNCs provide better mechanical and water vapor barrier properties.

The gelatin and starch have the characteristics properties of eco-friendly, safe, abundance, cost-effective, edible and thus can be used in combination to develop edible films. Additionally, the fabrication of smart edible films using starch-butanetetracarboxylic acid dianhydride-N-hydroxysuccinimide (SBN) cross-linked gelatin can provide improved surface hydrophobicity, tensile strength, elongation at break and is applicable for improved quality of postharvest shelf life [57]. The tensile strength of neat gelatin, 5% SBN-gelatin, 10% SBN-gelatin, 15% SBN-gelatin is $\sim 35.73 \pm 0.41$ MPa, 43.36 ± 0.38 MPa, 45.37 ± 0.88 MPa, 46.65 ± 0.63 MPa, respectively. The edible films based on quinoa protein, starch NPs, crude phenolic compound extracts (luria leaves/pomegranate peels) also provide enhanced packaging attributes with a safe packaging system for improved food product life [58]. Furthermore, the composite film based on banana starch, aloe vera, curcumin loaded starch NPs provides improved water vapor permeability and tensile strength due to the hydrophobic nature of curcumin [59]. Additionally, the composite film delivers control release profile of curcumin, which provides application in various food stuff. The mung bean-based native starch has smooth surface with oval shape, can be used to fabricate nanostarch using acid hydrolysis methods, having the average particle-size distribution of 141.772 nm. The biocomposite films based on nanostarch from mung bean (concentrations: 0.5, 1, 2, 5 and 10%) and native starch can be used as edible coating in food applications having renewable and biodegradable nature. Further, this specific biocomposite films provide improved film attributes such as (1) Burst strength increases from 943.56 ± 18.1 to 1265 ± 18.9 g; (2) Thickness of films increases from 0.043 ± 0.006 to 0.063 ± 0.006 mm; (3) Water vapor transmission rate (WVTR) decreases from $5.558 \times 10^{-3} \pm 0.25$ to $3.364 \times 10^{-3}\ g^{-2}\ s^{-1}$; and (4) Water solubility decreases from 37.99 ± 0.47 to 34.11 ± 0.40% [60]. The nanocomposite based on thermoplastic starch (glycerol as a plasticizer) and waxy maize starch provides strong interactions between filler materials and filler–matrix materials due to the hydrogen bonding [61]. The fabrication of starch films incorporating vacuum freeze-dried and spray-dried starch NPs provides denser films, enhanced film roughness, where the incorporation of starch NPs lowers the water vapor permeability (by 44%), glass transition temperature (by 4.3 °C) and crystallinity (by 23.5%), Young's modulus and toughness [62]. Additionally, the incorporation of starch NPs in the biocomposite films of starch offers increased storage moduli, loss moduli, and others [63]. Further, in Table 5.3, use of starch-based nanostructured materials in edible food packaging has been detailed for improved features of edible food packaging.

Table 5.3 Use of starch-based nanostructured materials in edible food packaging

Sl No.	Form of nanostarch	Other film components	Materials property	References
1.	STNCs (Fabrication process: Acid hydrolysis at 35 °C from waxy maize starch)	Pullulan Sorbitol (Plasticizers) (biocomposite edible films)	Increase in crystallinity with increased STNC Water uptake decreased with increasing filler content Improved Young's modulus and tensile strength	[55]
2.	Starch-butanetetracarboxylic acid dianhydride-*N*-hydroxysuccinimide (SBN) (a cross-linker)	Gelatin	Improved surface hydrophobicity Improved tensile strength and elongation at break Enhanced shelf life of peeled apple Is applicable for improved quality of postharvest shelf life	[57]

(continued)

Table 5.3 (continued)

Sl No.	Form of nanostarch	Other film components	Materials property	References
3.	Starch NPs	Quinoa protein Crude phenolic compound extracts (luria leaves/ pomegranate peels) (edible films)	Extend shelf life of food Good barrier properties against oxygen, water vapor, and carbon dioxide. Increased strength due to STNPs	[58]
4.	STNCs	Cross-linked cassava starch	• Can be used for preservation of Huangguan pears • Cross-linked cassava starch with 6% STNCs provides better mechanical and water vapor barrier properties • Inhibit peroxidase, polyphenol oxidase enzyme activities of pears.	[56]
5.	STNCs (fabrication process: Acid Hydrolysis of waxy maize starch granules using sulfuric acid)	Carboxymethyl chitosan	• Maximum tensile strength: 29 MPa • Water absorption and water vapor permeability can be improved using STNCs • The percentage elongation at break decreases with increased STNCs	[53]
6.	Starch NPs	Banana starch, aloe vera, curcumin (loaded in starch NPs)	Incorporation of curcumin reduces the water vapor permeability due to hydrophobic nature. Improved tensile strength due to incorporation of curcumin in the composite films.	[59]
7.	Nanostarch (concentrations: 0.5, 1, 2, 5 and 10%) (Source: Mung bean)	Native starch	• Renewable, biodegradable, and edible coating in food application. • Burst strength increases from 943.56 ± 18.1 to 1265 ± 18.9 g	[60]

(continued)

Table 5.3 (continued)

Sl No.	Form of nanostarch	Other film components	Materials property	References
			• Thickness of films increases from 0.043 ± 0.006 to 0.063 ± 0.006 mm • WVTR decreases from $5.558 \times 10^{-3} \pm 0.25$ to 3.364×10^{-3} g^{-2} s^{-1}	
8.	STNCs (fabricated via acid hydrolysis using sulfuric acid)	Lemon peel extract (ultrasonic extract)	Bioactive preservative coating on chicken fillets Improved quality of chicken fillets during 12 days cold storage	[54]

STNCs Starch nanocrystal, *NPs* Nanoparticles

5.10 Conclusion

The starch is extensively obtained from (1) Cereal grain seeds (maize, wheat, rice, sorghum); (2) Roots and tubers (potato, sweet potato, tapioca, arrowroot); and (3) Stems and pith (Sago). The available starchy foods are cereals, pasta, bread, rice, potatoes, beans, chestnuts, etc. In different categories of food preservation techniques and to improve food properties, starch and its various derivatives are also used. Starch NPs are utilized as a nanofiller material to develop biocomposites to modify mechanical and barrier properties. The STNCs are used in developing biocomposite films due to the crystalline nature for improved mechanical and barrier property. The use of plasticizers can improve the mechanical properties of starch; however, the hydrophilic nature of starch makes it sensitive toward moisture. In this regard, several modifications of starch-based films are required to act as a proper food packaging system.

Bibliography

1. Gutiérrez TJ, Morales NJ, Pérez E, Tapia MS, Famá L (2015) Physico-chemical properties of edible films derived from native and phosphated cush-cush yam and cassava starches. Food Packag Shelf Life 3:1–8. https://doi.org/10.1016/j.fpsl.2014.09.002
2. Das M, Mandal B, Katiyar V (2020) Environment-friendly synthesis of sustainable chitosan-based nonisocyanate polyurethane: a biobased polymeric film. J Appl Polym Sci. 137(36). https://doi.org/10.1002/app.49050

3. Maran JP, Sivakumar V, Sridhar R, Immanuel VP (2013) Development of model for mechanical properties of tapioca starch based edible films. Ind Crops Prod 42:159–168. https://doi.org/10.1016/j.indcrop.2012.05.011
4. Cazón P, Velazquez G, Ramírez JA, Vázquez M (2017) Polysaccharide-based films and coatings for food packaging: a review. Food Hydrocoll 68:136–148. https://doi.org/10.1016/j.foodhyd.2016.09.009
5. Das M, Mandal B, Katiyar V (2020) Sustainable routes for synthesis of poly (ε-Caprolactone): prospects in chemical industries. Adv Sustain Polym, 21–33. https://doi.org/10.1007/978-981-15-1251-3_2
6. Maran JP, Sivakumar V, Sridhar R, Thirugnanasambandham K (2013) Development of model for barrier and optical properties of tapioca starch based edible films. Carbohydr Polym 92 (2):1335–1347. https://doi.org/10.1016/j.carbpol.2012.09.069
7. Rompothi O, Pradipasena P, Tananuwong K, Somwangthanaroj A, Janjarasskul T (2017) Development of non-water soluble, ductile mung bean starch based edible film with oxygen barrier and heat sealability. Carbohydr Polym 157:748–756. https://doi.org/10.1016/j.carbpol.2016.09.007
8. Ali A, Xie F, Yu L, Liu H, Meng L, Khalid S, Chen L (2018) Preparation and characterization of starch-based composite films reinfoced by polysaccharide-based crystals. Compos Part B-Eng 133:122–128. https://doi.org/10.1016/j.compositesb.2017.09.017
9. Bradley EL, Castle L, Chaudhry Q (2011) Applications of nanomaterials in food packaging with a consideration of opportunities for developing countries. Trends Food Sci Technol 22 (11):604–610. https://doi.org/10.1016/j.tifs.2011.01.002
10. Pathakoti K, Manubolu M, Hwang HM (2017) Nanostructures: current uses and future applications in food science. J Food Drug Anal 25(2):245–253. https://doi.org/10.1016/j.jfda.2017.02.004
11. Karakelle B, Kian-Pour N, Toker OS, Palabiyik I (2020) Effect of process conditions and amylose/amylopectin ratio on the pasting behavior of maize starch: a modelling approach. J Cereal Sci 94:102998. https://doi.org/10.1016/j.jcs.2020.102998
12. Le Corre D, Bras J, Dufresne A (2010) Starch nanoparticles: a review. Biomacromol 11 (5):1139–1153. https://doi.org/10.1021/bm901428y
13. Lemos PV, Barbosa LS, Ramos IG, Coelho RE, Druzian JI (2019) Characterization of amylose and amylopectin fractions separated from potato, banana, corn, and cassava starches. Int J Biol Macromol 132:32–42. https://doi.org/10.1016/j.ijbiomac.2019.03.086
14. Wang S, Wang J, Yu J, Wang S (2014) A comparative study of annealing of waxy, normal and high-amylose maize starches: the role of amylose molecules. Food Chem 164:332–338. https://doi.org/10.1016/j.foodchem.2014.05.055
15. Vamadevan V, Bertoft E (2020) Observations on the impact of amylopectin and amylose structure on the swelling of starch granules. Food Hydrocoll 103:105663. https://doi.org/10.1016/j.foodhyd.2020.105663
16. He W, Wei C (2017) Progress in C-type starches from different plant sources. Food Hydrocoll 73:162–175. https://doi.org/10.1016/j.foodhyd.2017.07.003
17. Cornejo-Ramírez YI, Martínez-Cruz O, Del Toro-Sánchez CL, Wong-Corral FJ, Borboa-Flores J, Cinco-Moroyoqui FJ (2018) The structural characteristics of starches and their functional properties. CyTA-J Food 16(1):1003–1017. https://doi.org/10.1080/19476337.2018.1518343
18. Zhu J, Zhang S, Zhang B, Qiao D, Pu H, Liu S, Li L (2017) Structural features and thermal property of propionylated starches with different amylose/amylopectin ratio. Int J Biol Macromol 97:123–130. https://doi.org/10.1016/j.ijbiomac.2017.01.033
19. Amit SK, Uddin MM, Rahman R, Islam SR, Khan MS (2017) A review on mechanisms and commercial aspects of food preservation and processing. Agric Food Secur 6(1):51. https://doi.org/10.1186/s40066-017-0130-8
20. Costa MJ, Maciel LC, Teixeira JA, Vicente AA, Cerqueira MA (2018) Use of edible films and coatings in cheese preservation: opportunities and challenges. Food Res Int 107:84–92. https://doi.org/10.1016/j.foodres.2018.02.013

21. Industrial Starch Market by type (native, starch derivatives & sweeteners), source (corn, wheat, cassava, potato), application (food, feed, paper making & corrugation, pharmaceutical), form (dry, liquid), and region—global forecast to 2022. Accessed: June 2020 https://www.marketsandmarkets.com/Market-Reports/industrial-starch-market-104251261.html
22. Industrial starch market: global industry analysis and forecast 2017–2025. Accessed June 2020 https://www.persistencemarketresearch.com/market-research/industrial-starch-market.asp
23. González-Cruz L, Montañez-Soto JL, Conde-Barajas E, Negrete MDLLX, Flores-Morales A, Bernardino-Nicanor A (2018) Spectroscopic, calorimetric and structural analyses of the effects of hydrothermal treatment of rice beans and the extraction solvent on starch characteristics. Int J Biol Macromol 107:965–972. https://doi.org/10.1016/j.ijbiomac.2017.09.074
24. Bento JAC, Ferreira KC, de Oliveira ALM, Lião LM, Caliari M, Júnior MSS (2019) Extraction, characterization and technological properties of white garland-lily starch. Int J Biol Macromol 135:422–428. https://doi.org/10.1016/j.ijbiomac.2019.05.141
25. da Silva LR, de Carvalho CWP, Velasco JI, Fakhouri FM (2020) Extraction and characterization of starches from pigmented rices. Int J Biol Macromol 156:485–493. https://doi.org/10.1016/j.ijbiomac.2020.04.034
26. Díaz A, Dini C, Viña SZ, García MA (2016) Starch extraction process coupled to protein recovery from leguminous tuberous roots (Pachyrhizus ahipa). Carbohydr Polym 152:231–240. https://doi.org/10.1016/j.carbpol.2016.07.004
27. Li Y, Wu Z, Wan N, Wang X, Yang M (2019) Extraction of high-amylose starch from Radix Puerariae using high-intensity low-frequency ultrasound. Ultrason Sonochem 59:104710. https://doi.org/10.1016/j.ultsonch.2019.104710
28. Hernández-Carmona F, Morales-Matos Y, Lambis-Miranda H, Pasqualino J (2017) Starch extraction potential from plantain peel wastes. J Environ Chem Eng 5(5):4980–4985. https://doi.org/10.1016/j.jece.2017.09.034
29. Silva EMS, Peres AEC, Silva AC, Leal MCDM, Liao LM, de Almeida VO (2019) Sorghum starch as depressant in mineral flotation: part 1–extraction and characterization. J Mater Res Technol 8(1):396–402. https://doi.org/10.1016/j.jmrt.2018.04.001
30. Hao Y, Chen Y, Li Q, Gao Q (2018) Preparation of starch nanocrystals through enzymatic pretreatment from waxy potato starch. Carbohydr Polym 184:171–177. https://doi.org/10.1016/j.carbpol.2017.12.042
31. Dai L, Zhang J, Cheng F (2019) Succeeded starch nanocrystals preparation combining heat-moisture treatment with acid hydrolysis. Food Chem 278:350–356. https://doi.org/10.1016/j.foodchem.2018.11.018
32. Zhou L, Fang D, Wang M, Li M, Li Y, Ji N, Dai L, Lu H, Xiong L, Sun Q (2020) Preparation and characterization of waxy maize starch nanocrystals with a high yield via dry-heated oxalic acid hydrolysis. Food Chem 318:126479. https://doi.org/10.1016/j.foodchem.2020.126479
33. Velásquez-Castillo LE, Leite MA, Ditchfield C, do Amaral Sobral PJ, Moraes ICF (2020) Quinoa starch nanocrystals production by acid hydrolysis: kinetics and properties. Int J Biol Macromol 143:93–101. https://doi.org/10.1016/j.ijbiomac.2019.12.011
34. LeCorre D, Vahanian E, Dufresne A, Bras J (2012) Enzymatic pretreatment for preparing starch nanocrystals. Biomacromol 13(1):132–137. https://doi.org/10.1021/bm201333k
35. do Prado Cordoba L, Ribeiro LS, Rosa LS, Lacerda LG, Schnitzler E (2016) Effect of enzymatic treatments on thermal, rheological and structural properties of pinhão starch. Thermochim Acta 642:45–51. https://doi.org/10.1016/j.tca.2016.08.020
36. Kim JY, Park DJ, Lim ST (2008) Fragmentation of waxy rice starch granules by enzymatic hydrolysis. Cereal Chem 85(2):182–187. https://doi.org/10.1094/CCHEM-85-2-0182
37. Le Corre D, Angellier-Coussy H (2014) Preparation and application of starch nanoparticles for nanocomposites: a review. React Funct Polym 85:97–120. https://doi.org/10.1016/j.reactfunctpolym.2014.09.020

38. Ma X, Jian R, Chang PR, Yu J (2008) Fabrication and characterization of citric acid-modified starch nanoparticles/plasticized-starch composites. Biomacromol 9(11):3314–3320. https://doi.org/10.1021/bm800987c
39. Hebeish A, El-Rafie MH, El-Sheikh MA, El-Naggar ME (2014) Ultra-fine characteristics of starch nanoparticles prepared using native starch with and without surfactant. J Inorg Organomet Polym Mater 24(3):515–524. https://doi.org/10.1007/s10904-013-0004-x
40. Ren L, Jiang M, Wang L, Zhou J, Tong J (2012) A method for improving dispersion of starch nanocrystals in water through crosslinking modification with sodium hexametaphosphate. Carbohydr Polym 87(2):1874–1876. https://doi.org/10.1016/j.carbpol.2011.08.070
41. Alkanawati MS, Wurm FR, Thérien-Aubin H, Landfester K (2018) Large-scale preparation of polymer nanocarriers by high-pressure microfluidization. Macromol Mater Eng 303 (1):1700505. https://doi.org/10.1002/mame.201700505
42. Liu D, Wu Q, Chen H, Chang PR (2009) Transitional properties of starch colloid with particle size reduction from micro-to nanometer. J Colloid Interface Sci 339(1):117–124. https://doi.org/10.1016/j.jcis.2009.07.035
43. Marques AP, Pirraco RP, Reis RL (2008) Biocompatibility of starch-based polymers. In: Natural-based polymers for biomedical applications. Woodhead Publishing, pp 738–760. https://doi.org/10.1533/9781845694814.6.738
44. Marques AP, Reis RL, Hunt JA (2002) The biocompatibility of novel starch-based polymers and composites: in vitro studies. Biomaterials 23:1471–1478. https://doi.org/10.1016/S0142-9612(01)00272-1
45. Mendes SC, Reis RL, Bovell YP, Cunha AM, van Blitterswijk CA, de Bruijn JD (2001) Biocompatibility testing of novel starch-based materials with potential application in orthopaedic surgery: a preliminary study. Biomaterials 22:2057–2064. https://doi.org/10.1016/S0142-9612(00)00395-1
46. Wu C, Wang Z, Zhi Z, Jiang T, Zhang J, Wang S (2011) Development of biodegradable porous starch foam for improving oral delivery of poorly water soluble drugs. Int J Pharm 403:162–169. https://doi.org/10.1016/j.ijpharm.2010.09.040
47. Zhao R, Torley P, Halley PJ (2008) Emerging biodegradable materials: starch-and protein-based bio-nanocomposites. J Mater Sci 43:3058–3071. https://doi.org/10.1007/s10853-007-2434-8
48. Wootton M, Manatsathit A (1983) The influence of molar substitution on the water binding capacity of hydroxypropyl maize starches. Starch Stärke 35:92–94. https://doi.org/10.1002/star.19830350306
49. Hoover R, Sosulski F (1986) Effect of cross-linking on functional properties of legume starches. Starch Stärke 38:149–155. https://doi.org/10.1002/star.19860380502
50. Godbillot L, Dole P, Joly C, Rogé B, Mathlouthi M (2006) Analysis of water binding in starch plasticized films. Food Chem 96:380–386. https://doi.org/10.1016/j.foodchem.2005.02.054
51. Shah U, Naqash F, Gani A, Masoodi FA (2016) Art and science behind modified starch edible films and coatings: a review. Compr Rev Food Sci Food Saf 15:568–580. https://doi.org/10.1111/1541-4337.12197
52. Xie F, Pollet E, Halley PJ, Averous L (2013) Starch-based nano-biocomposites. Progress Polym Sci 38:1590–1628. https://doi.org/10.1016/j.progpolymsci.2013.05.002
53. Duan B, Sun P, Wang X, Yang C (2011) Preparation and properties of starch nanocrystals/carboxymethyl chitosan nanocomposite films. Starch Stärke 63:528–535. https://doi.org/10.1002/star.201000136
54. Alizadeh Z, Yousefi S, Ahari H (2019) Optimization of bioactive preservative coatings of starch nanocrystal and ultrasonic extract of sour lemon peel on chicken fillets. Int J Food Microbiol 300:31–42. https://doi.org/10.1016/j.ijfoodmicro.2019.04.002
55. Kristo E, Biliaderis CG (2007) Physical properties of starch nanocrystal-reinforced pullulan films. Carbohydr Polym 68:146–158. https://doi.org/10.1016/j.carbpol.2006.07.021

56. Dai L, Zhang J, Cheng F (2020) Cross-linked starch-based edible coating reinforced by starch nanocrystals and its preservation effect on graded Huangguan pears. Food Chem 311:125891. https://doi.org/10.1016/j.foodchem.2019.125891
57. Tao F, Shi C, Cui Y (2018) Preparation and physicochemistry properties of smart edible films based on gelatin–starch nanoparticles. J Sci Food Agric 98:5470–5478. https://doi.org/10.1002/jsfa.9091
58. Aboul-Anean HED (2018) Using quinoa protein and starch nano particles to produce edible films. J Nut Health Food Eng 8:297–308
59. Nieto-Suaza L, Acevedo-Guevara L, Sánchez LT, Pinzón MI, Villa CC (2019) Characterization of Aloe vera-banana starch composite films reinforced with curcumin-loaded starch nanoparticles. Food Struct 22:100131. https://doi.org/10.1016/j.foostr.2019.100131
60. Roy K, Thory R, Sinhmar A, Pathera AK, Nain V (2020) Development and characterization of nano starch-based composite films from mung bean (Vigna radiata). Int J Biol Macromol 144:242–251. https://doi.org/10.1016/j.ijbiomac.2019.12.113
61. Angellier H, Molina-Boisseau S, Dole P, Dufresne A (2006) Thermoplastic starch—waxy maize starch nanocrystals nanocomposites. Biomacromol 7:531–539. https://doi.org/10.1021/bm050797s
62. Shi AM, Wang LJ, Li D, Adhikari B (2013) Characterization of starch films containing starch nanoparticles: part 1: physical and mechanical properties. Carbohydr Polym 96:593–601. https://doi.org/10.1016/j.carbpol.2012.12.042
63. Shi AM, Wang LJ, Li D, Adhikari B (2013) Characterization of starch films containing starch nanoparticles. part 2: viscoelasticity and creep properties. Carbohydr Polym 96:602–610. https://doi.org/10.1016/j.carbpol.2012.10.064