Chapter

Advances and Trends in the Physicochemical Properties of Corn Starch Blends

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Abstract

Corn starch is one of the most widely used biopolymers in the world for various applications, due to its high production, renewable, low cost, non-toxic, biodegradable and provide great stereochemical diversity by presenting a complex structure with unique qualities that they depend on multiple factors to obtain special properties for a specific use and/or of interest. From the synthesis of the starch granule to its extraction for its subsequent use, it promotes innovative characteristics, presenting infinite functionalities applicable and/or as a substitute for synthetic polymers. However, some limitations of hydrophilicity, thermal and mechanical properties, rapid degradability and strong intra and intermolecular bonds of the polymer chains make their use difficult in the medium and long term. Enzymatic, chemical and physical methods continue to be used today, creating by-products such as polluting waste and which can be costly. Therefore, the polymeric modification of the starch granule is necessary to mitigate limitations and by-products, currently the use of starch blends is a promising trend to produce new and innovative desirable properties. This chapter describes the advances and trends in the physicochemical properties of corn starch blends *Zea mays* L. as a potential material, leader for its attractive properties and benefits that it has to offer, demonstrating that when combined with other starches from different botanical sources and/or molecular structure present unique and unequaled synergisms.

Keywords: Corn, Starch, Blends, Extrusion, Microencapsulation

1. Introduction

Corn (*Zea mays* L.) is the cereal with the highest production in the world due to the amount of nutrients that it provides beneficial for the consumer. Starch is the main component of the energy source precursor corn kernel. The main polysaccharides that make up starch are: Amylose is made up of α-D-glucose units linked by α (1,4) glucosidic bonds, while amylopectin is a branched polymer formed by linked α-D-glucose units by α (1- > 4) glucosidic bonds with branching points in the form of α (1,6) bonds. The amylose and amylopectin molecules form alternating stacks of crystalline amorphous lamellae and semicrystalline growth rings, originating highly organized granules that may differ with respect to the genotype of the botanical source of extraction, amylose is dispersed over the entire structure of amylopectin [1]. Currently corn starch is used as an emulsifying agent, encapsulant, stabilizer, colloidal gelling agent, water retention agent, among other uses due to the unique physicochemical characteristics that it presents, in addition to being accessible, non-toxic and having high yields at low cost production [2].

2. Corn starch

Corn is one of the staple foods and is used as an industrial by-product. The corn grain comes from the independent fruit called caryopsis that is inserted in the cylindrical rachis "ear", each grain or seed is limited by the number of grains per row and rows per ear. The pericarp (wall of the ovary) and testa (seed coat) join to form the wall of the ear. The corn kernel is made up of 3 main parts: "embryo", "endosperm" and "wall of the fruit". The amount of kernels produced on each ear and the number of ears that grow is generally confirmed when pollinating [3, 4]. In addition to the different derivatives of corn such as corn oil, gluten, syrup, dextrose, ethanol among others. Corn starch provides ideal characteristics for various industrial applications in the textile, food, pharmaceutical, construction fields, among others. It is composed mainly of amylose/amylopectin in different proportions and polymeric organizations. These two components of starch represent approximately ≥99% of starch by dry weight. Commonly the conformation is 75% amylopectin and 25% amylose. The polymeric structure of amylopectin provides the morphology of the granule. Amylopectin is made up of -D-glucopyranosyl chains, which are highly branched and the chains are connected to each other by 1,4 bonds, with almost 6% of 1,6 bonds forming branch points. Amylose is found in small amounts compared to amylopectin. It is an unbranched unit with 1,4-linked glucopyranosyl units, although it does not have branches, but there are some molecules that are slightly branched with 1,6-linkages. Amylopectin is the main molecule that causes the various changes on the physicochemical properties of the starch granule, changing the rheological, hygroscopic, retrogradation and leaching properties of amylose, generating new structural conformations, glass transition and maximum viscosity. On the other hand, amylose (leaching) also has a directly proportional effect on the changes that amylopectin presents, due to the response factors applied to starch [5].

Starch in the native state (without amylose/amylopectin structural modification) is available as a reserve carbohydrate in many parts of plants, including roots, tubers, cereals, and seeds. **Figure 1** presents a proposed scheme on the biosynthesis of corn starch. In general, the main enzymes for starch biosynthesis include mainly ADP-glucose pyrophosphorylases (AGPases), granule-bound starch synthases (GBSS), soluble starch synthases (SS), starch branching enzymes (BE) and starch debranching enzymes (DBE). AGPase catalyzes the first step reaction of starch biosynthesis by converting glucose 1-phosphate (Glc-1-P) and ATP to ADP-Glc and inorganic pyrophosphate (PPi) in amyloplasts. GBSS and SSS are responsible for synthesizing amylose and amylopectin, respectively. SBE introduces a branched structure by cleaving the internal chains of α-1,4-glucan and transferring the chain

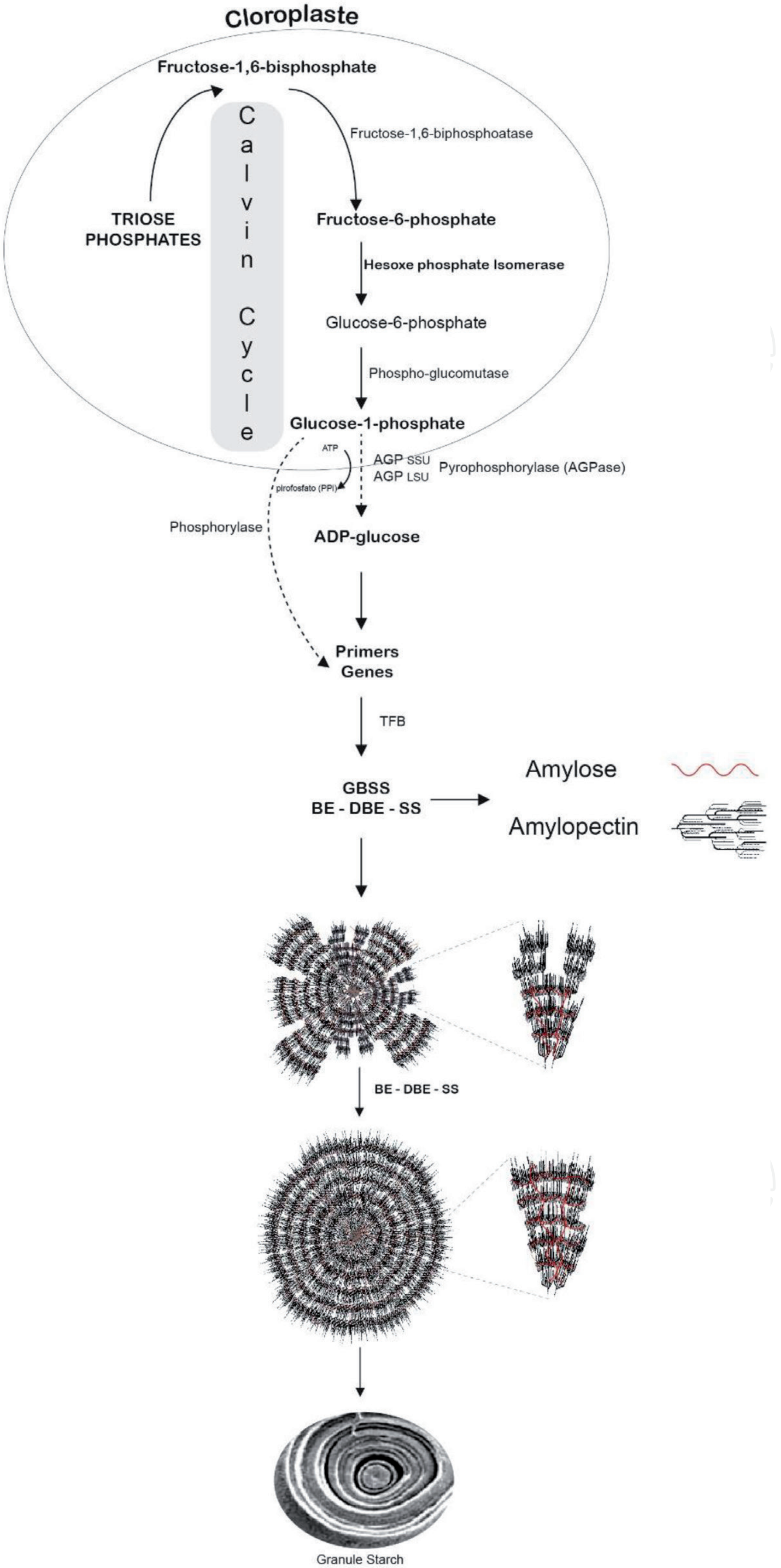

Figure 1.
Corn starch biosynthesis scheme.

segment of six or more glucose units to the C6 position of a glucosyl residue of another glucan chain. DBEs, through their α-1,6-hydrolytic activity, act on highly branched pre-amylopectin, generating polymodal distributed end chains of amylopectin. However, recent research has shown that by modifying the plant gene, variations in the content, distribution, size and polymeric organization of amylose and amylopectin are obtained [6–8]. AGPase catalyzes the first key regulatory step in the starch biosynthetic pathways present in all higher plants that produce ADP-Glc and pyrophosphate (PPi) from Glc-1-P and ATP. Plant AGPases exist as a heterotetramer (α2β2) composed of two large (LSU) and two small (SSU) subunits with slightly different molecular masses [9, 10]. SSUs are responsible for the catalytic activity of the enzyme complex, while LSU is believed to modulate enzymatic regulatory properties that increase the allosteric response of SSU to 3-phosphoglyceric acid (3-PGA) and inorganic phosphate (Pi) [9, 11]. AGPase activity is localized to both plastids and the endosperm cytosol of cereals, in contrast to other plant species where it has been reported to occur only in plastids [12]. In a previously reported subcellular fractionation experiment using corn endosperm, the highest AGPase activity was detected in the cytosol [13]. Furthermore, the genes responsible for the shrunk2 and brittle2 starch-deficient maize kernel phenotypes encode the endosperm-specific cytosolic LSU and SSU isoforms, respectively [14, 15]. This information is an indicator that plastid AGPase, by itself, is not sufficient to support normal starch biosynthesis processes in cereal endosperm, therefore, some researchers suggest that it is possible that plastid starch phosphorylase (Pho1) play an important role in the formation of primers to complete starch biosynthesis in the endosperm. Recent advances still trying to understand the functions of individual enzyme isoforms have provided new insights into how linear polymer chains (amylose) and branched bonds (amylopectin) are synthesized in cereals. Let us remember that both polysaccharides are made up of D-glucose chains linked by α (1–4) bonds. Amylose is essentially linear with α (1–4) bonds, while amylopectin is highly branched through α (1–6) bonds. Amylopectin forms type A and B polymorphic crystals that influence the arrangement of its double helices. Type A crystals produce relatively compact helices with a lower proportion of water, while type B crystals give rise to a more open structure containing a hydrated helical nucleus. X-ray diffraction studies allow us to know this type of crystal arrangements [16]. These conformations will always be different depending on the type of botanical source (TFB), as well as the enzymes involved in the formation of amylose and amylopectin.

The functional and physicochemical properties of corn starch are influenced by the amylose/amylopectin ratio, its chain length distribution and the presence of complexes in lower proportions with lipids/proteins. In its native form, corn starch has limited applications due to its low resistance to extreme processing conditions, shear, insolubility to water at room temperature, hygroscopicity among others, which are frequently found in the industry. Therefore, at present various modification techniques have been implemented that can be achieved by enzymatic, genetic, chemical, physical methods or a combination of some of these methods, which will allow a modification, mainly on the structure of amylopectin to obtain a functional starch that can overcome deficiencies and increase its usefulness for various industrial applications [17].

3. Starch blends

The use of different techniques to modify the polymeric structure of starch unfortunately have disadvantages, it can have high costs due to the use of reagents, some processes take long periods of time, low yields can generate residues that could affect the environment. Therefore, the proposals to use starch blends that promote new physicochemical characteristics that can replace conventional methods, trends that are diversifying unique properties by combining starches from different botanical sources [18]. Physical treatments are considered ecological friendly to the environment due to the absence of chemical agents and/or concentrated alkaline/acid solutions. It's essential to know the physicochemical properties of each starch to obtain the best combination in order to focus on the application, innovation or continuous improvement of some industrial type product.

3.1 Granule size

The blends of starches with different granule size and amylose content contribute to new molecular interactions between the amylose/amylopectin contents presenting significant changes in the physicochemical properties (e.g. rheological, swelling power, gel, solubility, viscosity among others), which are attributed to the content of amylose, chain length and retrogradation [18–20].

The biofilms that are formed from starch are a very promising option to avoid the excessive use of plastic (polyethylene, vinyl chloride, polystyrene and urea formaldehyde) and low and/or no deterioration on the environment. Unfortunately, with the population and industrial increase, the use of plastics continues to increase year after year, which generates millions of tons of waste after use. Polyethylene degradation is highly influenced by the biotic and abiotic environment, thus limiting effective degradation. Currently, through various investigations, the development of plastics for packaging from biodegradable materials is being promoted, using starch as the main raw material [21, 22]. The wide variety of research on the use of starches from various botanical sources (e.g. potato, corn, wheat, tapioca, rice and others) and its low cost together with comparable characteristics for film formation have shown that it is an efficient packaging raw material and a possible substitute for polyethylene, however, there are still physicochemical properties that are still under experimentation, taking into account the permeability to water vapor, mechanical properties, glass transition and hydrophobicity. The film formation process from starch granules has been described by different authors, the quality of the film is greatly affected by the amylose/amylopectin/plasticizer (glycerol) ratio, the latter being the most widely used. The content of amylose/amylopectin, a variation in the intrinsic properties of the film can be observed due to the deviation in the content of phosphorus, molar mass of starch and the biochemistry of amyloplast and chloroplast [23]. Corn is a predominant source of starch (65%) produces a film with a higher percentage of elongation, better oxygen barrier properties and a high elastic modulus, in addition [24]. The formation of biofilms from blends of cassava/corn starch with cellulose was shown to have a hydrophobic effect by reducing the affinity of starch films with water and considerably reduced the rate of permeability to water vapor, thus improving their properties. In addition, the amylose content promotes the production of a more hydrophobic film, due to the strong interactions of intermolecular bonds with glycerol [25]. New techniques for incorporating particles onto others, as reported by Farrag, et al. [26], I present reported that they prepared starch microparticles with donut-shaped morphology from two different botanical origins (type A and C for corn and pea starch granules, respectively) by means of a simple hydroalcoholic heat treatment. The donut-shaped microparticles were loaded onto films of the same botanical origin, generating greater thermal stability of the films produced. In addition, adjusting the percentage of microparticles in the thermoplastic films allowed to supply the desired amount of oxygen and water vapor to the packaged food. This is very important to keep packaged foods fresh and healthy for as long as possible. Emulsions are systems that are characterized by presenting small dispersed droplets of an immiscible liquid phase in another liquid phase, based on many applications in different industries (eg food, nutraceutical, cosmetic, hygiene, detergents, pharmaceutical and medical), however, to stabilize these emulsifying systems, synthetic surfactants (Tweens 20/60/80) or emulsifiers of animal origin (albumin/casein) are used [27]. However, they have disadvantages in their formulation because they generate foam retention due to the trapped oxygen and interactions with other suspended molecules and even the surfactant that is not compatible, an emulsion being key for the production of various food and pharmaceutical products, it is necessary to produce emulsions with solid particles of vegetable origin to stabilize the emulsions, which is called Pickering emulsions [28]. Compared to surfactant stabilized emulsions, Pickering emulsions tend to be more stable against Ostwald ripening and coalescence. Currently, starch and cellulose are used to create Pickering emulsions. Starch for its different physicochemical properties (generally recognized as safe, non-allergenic, abundant and cheap). Unfortunately, starches are still being modified to make Pickering-type emulsions, the most widely used is succinate with octenyl succinic anhydride (OSA) reagent for emulsion production. So far, the information on Pickering starch emulsions is very scattered. The links between the manufacture of Pickering emulsions and their applications are largely absent. The lack of such links seriously undermines our research efforts to better utilize emulsions for practical applications [29]. Native starch granules are not suitable for creating stable Pickering emulsions. The starch is modified to be suitable for making a Pickering emulsion. However, future trends suggest using starch blends of granule size ≤10 μm that can be compatible with starch concentration, oil and water volume, pH, ionic strength, storage conditions, processing and presence of other components for obtain a drop size (1–100 μm) [29]. Amaranth starch has shown to have sizes ≤2 μ, which is a potential candidate to produce emulsifying systems without modifying the molecular structure by chemical agents, however, physical modifications will have to be used (e.g. temperature, pH, pressure, radiation, homogenization at high revolutions among others) to obtain favorable and applicable results [30].

Grinding on native starch granules to reduce the particle size, proved to be favorable to elaborate a Pickering emulsion system [31]. The high pressure treated starch chips and ground starch particles are partially gelatinized. They can represent a mixture of rigid particle and flexible polymer model systems in emulsions. The deformability of the starch particles can be modified in situ in Pickering emulsion systems. Heating Pickering emulsions can gelatinize starch granules to different degrees. Heating can make the boundaries between adjacent particles indistinct. During heating, some amylose and amylopectin molecules leak out of the swelling granules, causing a stabilizing layer of starch granules, becoming a layer of swollen granules interpenetrated with leached starch (amylose) polymers. In this type of emulsion systems with partially gelatinized starch granules, rigid particles (granules) and flexible polymers (leached starch molecules) coexist [32, 33]. In general, the droplet size of Pickering emulsions can be adjusted using compatible starch blends, different sizes, use of physical methods, suitable starch concentrations, and processing methods.

3.2 Extrusion

Extrusion is a continuous processing method, it involves high pressure and temperature in a short time. Its main function is to mix various components. The extrusion process allows the gelatinization of the starch, the denaturation of the proteins and even the molecular degradation due to the effects of high shear depending on the screw to be used, which in turn affects the physicochemical properties of the extrudates. Many studies have been conducted to explore the relationships between extrusion processing parameters and non-food starch characteristics in order to improve processing control [34]. However, little scientific evidence has attempted to understand the relationships between the physicochemical properties of extrudates and the molecular characteristics of starch after the extrusion process using starch blends, because using starches in the native state affects the bostwick flow (viscosity and/or consistency) on the extruder barrel causing a process obstruction, therefore, previous parameters for an excellent extrusion must be considered, such as the amount of starch moisture, the temperatures of each zone of the extruder, as well as the time and type shear stress, which is crucial to achieving product quality and developing novel products [35]. The use of corn starch/cassava blends provides different degrees of gelatinization and some existing air microcells in the extrudates, attributing this effect to the extension of the puff and the fine structures of the extrudates when they were exposed to different temperatures, residence times. in the extruder and the amount of moisture present in the starch sample [36].

3.3 Encapsulation

The microencapsulation process by spray drying method allows the use of a large number of wall materials. It is essential to know the type of starch to use, it must present characteristics such as high solubility, low swelling power and viscosity, thus allowing effective encapsulation, since it can influence the properties of the emulsion, the retention of active principle, flavor and the end product shelf life. Currently there are no reports of works in which a mixture of two or more starches is implemented to be used as wall material due to the increase in viscosity, however, new trends such as using blends of porous starches, which are naturally derived from starch native by physical, chemical or biological methods. There are pores, holes and/or openings with diameters less than one micron in the structural lattices, through which molecules with smaller particle size can enter the polymeric structure and become encapsulated. The use of these possible starch blends will be an option and research topic to avoid conventional modifications on the structure of the starch, being an environmentally friendly option and without remnants of solutions with chemical reagents [37].

4. Conclusions and future trends for corn starch

Corn starch is a natural biopolymer, it has multiple physicochemical properties, an option to replace most of the synthetic polymers in the future to reduce pollution and preserve the environment. The use of blends with other starches from different botanical sources and even other biopolymers of different molecular structure (e.g. pectin, cellulose, chitosan, gelatin, alginate, hydroxyapatite, protein) are tendencies to avoid the use and generation of chemical residues that affect the environment and increase production prices. These blends are promising that demonstrate in this chapter a biocompatibility and diversity of physical properties friendly with the environment without affecting third parties. The challenge to be overcome is to completely replace the most widely used synthetic polymers around the world, through the development of biofilms based on corn starch, and how to improve the mechanical, hydrophobic and permeable properties is still being investigated. In addition, cornstarch can be used to improve filtration materials, absorbents, transport, diffusibility, hydrogels, paper, adhesives, biofuels. Therefore, the future of cornstarch blends will continue to be an encouraging proposition to generate high-value products for novel applications in various areas.

Conflict of interest

The authors declare that they have no conflict of interest.

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