Starch: Botanical Sources and Modification Through Extrusion

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Starch, the primary storage carbohydrate found throughout the plant kingdom, is a vital energy source in the human diet. It is synthesized within plastids in both photosynthetic and non-photosynthetic cells, forming insoluble, semi-crystalline granules. These granules consist of amylose and amylopectin, two crucial components. Although starch is widely used in various sectors, including food, pharmaceuticals, and industry, its functional properties vary significantly between plant species, leading to challenges in processing and nutrition. Globally, the industrial starch market is valued around 90 billion USD in 2024 at a compound annual growth rate (CAGR) of 5.8%.

Understanding the intricate structure of starch, particularly the roles of amylose and amylopectin, is essential. Both are homopolysaccharides made of α-D-glucose units and feature specific glycosidic linkages. Amylopectin, the predominant component, has a highly branched structure that gives rise to the semi-crystalline nature of starch granules. Despite its significance, native starch has limitations such as poor solubility, retrogradation, and high viscosity after gelatinization. To overcome these limitations and unleash its full potential, diverse starch modification techniques have been developed.

Amylose & Amylopectin

Amylose and amylopectin, the structural pillars of starch, are both composed of α-D-glucose units. Amylose consists of linear chains linked by α-1,4-glycosidic bonds, while amylopectin is highly branched due to additional α-1,6-glycosidic linkages at branching points. The heavily branched structure of amylopectin forms crystalline lamellae interspersed with amorphous regions. Amylopectin's intricate architecture arises from multiple short chains, each containing α-(1,4)-linked D-glucose residues and interconnected through α-(1,6)-linkages. The ratio of amylose to amylopectin varies among plant genotypes, impacting the granule's properties. These granules, stored in different plant parts, exhibit wide variations in size, shape, and composition, influenced by the plant's tissue and origin.

Characteristics of Starch Granules

Starch granules, found in various plant parts, exhibit diverse characteristics. Ranging from less than 1 µm to over 100 µm, these granules can assume spherical, oval, discoid, polygonal, angular, or irregular shapes. The size, shape, structure, and composition of starch granules are intricately linked to the plant's tissue and organ. Understanding these characteristics is pivotal for tailoring starch for specific applications, addressing challenges related to solubility, viscosity, and thermal stability. (Apriyanto *et al.*, 2022).

Need for Starch Modification

Despite its versatility, native starch faces inherent limitations, hindering its widespread industrial applications. Issues such as poor solubility, retrogradation (the tendency to revert to a more ordered state upon cooling), syneresis (release of water after gel formation), thermal decomposition, low resistance to shear stress and high viscosity post-gelatinization pose challenges. To overcome these limitations and harness starch's potential in various industries, diverse modification techniques have been developed. These methods aim to enhance solubility, stability, and functionality, making starch more adaptable to a myriad of applications, from food to pharmaceuticals. By modifying starch, researchers and industries are working towards unlocking its full potential, revolutionizing its applications and ensuring it remains a cornerstone biomaterial in a rapidly evolving world.

The major market drivers for application of starch in industries include:

1) The multiple functionalities of starch and its derivatives that can be tailored for use in a diverse range of industries,

2) Increasing demand for biodegradable plastics or packaging materials

3) Rising avenues of starch in various non-food applications, and

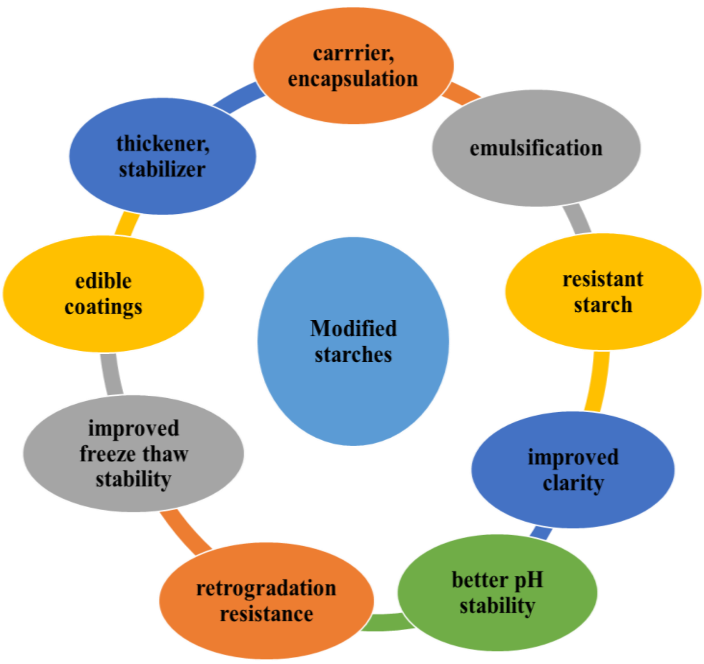
4) Increased availability of alternative sources of starch.

Modified starches as food additives

As per Codex standards, the chemically modified starches are approved as permitted food additives and are assigned with E-numbers. They are regulated under the terms of the EC Miscellaneous Additives Directive 95/2/EC, on food additives other than colours and sweeteners. Under the provisions of this Directive, modified starches have been defined as 'substances obtained by one or more chemical treatments of edible starch, which may have undergone a physical or enzymatic treatment and may be acid or alkali thinned or bleached'. The E numbers for modified starches are as follows

E1404	Oxidised starch
E1410	Monostarch phosphate
E1412	Distarch phosphate
E1413	Phosphated distarch phosphate
E1414	Acetylated distarch phosphate
E1420	Acetylated starch
E1422	Acetylated distarch adipate
E1440	Hydroxypropyl starch
E1442	Hydroxypropyl distarch phosphate
E1450	Starch sodium octenyl succinate
E1451	Acetylated oxidised starch

Food Applications of Modified Starches



Non-food applications of modified starches

Modified starches are important in the fields of paper making, textiles, packaging, regenerative medicine, 3 D printing, nanotechnology etc.

Botanical Sources of Starch

Starch is sourced from common crop plants such as corn, wheat, cassava, sweet potato, rye, barley, oats, rice, and pulses. Additionally, novel sources, including medicinal plants and fruits, contribute to starch production. (Table 1 & 2)

Type of Modification and their Applications:

Starch modification is a pivotal process in the food industry, enhancing starch's functional versatility in various products through diverse techniques. Physical modifications, including extrusion for altered texture and heat-moisture treatment for environmentally friendly films, find applications in noodles, convenience foods, and sauces. Chemical modifications such as cross-linking and acetylation provide stability and solubility, utilized in coatings, confectionery, and emulsion stabilizers. Enzymatic modifications like amylase treatment reduce viscosity for gelling agents, while genetic modifications engineer starch compositions for a wide range of applications. Dual modifications, combining physical and chemical methods, yield multifunctional starch used in diverse food products like puddings and frozen foods. These modified starches continue to innovate the food industry, meeting various consumer demands by enhancing texture, stability, and overall quality in products ranging from noodles to low-calorie beer and beyond. One of the major restraints to industrial starch applications is the intensive use of water and wastewater pollutants generated during the processing of starch which impact sustainable production of products downstream. Physical modification processes like heat mediated modification and extrusion processing offer some respite to these problems.

Extrusion Process

Extrusion disrupts the molecular order within starch granules by subjecting a starch suspension in water to temperatures exceeding the gelatinization temperature (TG). Gelatinization, a pivotal step, involves the irreversible destruction of the crystalline order within starch granules. Gelatinization, influenced by factors such as moisture content, pH, and pressure, precedes irreversible changes in starch properties. During extrusion, the crystallinity of corn starch decreases gradually with increasing moisture content, leading to enhanced gelatinization and granule expansion. Extrusion also affects proteins, lipids, and non-starch polysaccharides, forming a complex matrix with improved nutritional and functional properties (Yang *et al.*, 2020; Zhang *et al.*, 2015). Extrusion offers versatility in processing, low-cost requirements, the production of high-quality products, energy efficiency, and environmental friendliness.

Effect of Extrusion on Gelatinization

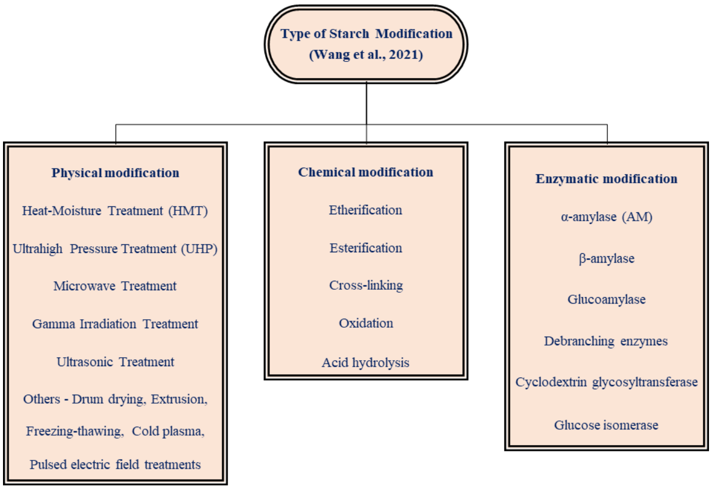
Gelatinization, a critical aspect of the extrusion process, involves the destruction of the crystalline regions of starch. Extrusion significantly increases the water absorption of starch, denoting enhanced gelatinization. Higher moisture content in raw corn starch facilitates water absorption, leading to increased gelatinization and decreased crystallinity. The gelatinization process is accompanied by the destruction of the crystal structure and the dissociation of amylopectin double helices. Extrusion-induced gelatinization is influenced by both temperature and moisture content, leading to profound structural changes in starch granules (Wang et al., 2021).

Effect on Starch Degradation

During extrusion, starch degradation is influenced by factors such as temperature, pressure, and shear forces. Extrusion-induced starch degradation facilitates interactions with other components, including citric acid anhydride, leading to cross-linking in starch citrate (Ye et al., 2019). Additionally, extrusion disrupts the integrity of starch granules while preserving certain characteristics desirable for sensorial and nutritional acceptance, making it a promising technology in the food industry (Arslan et al., 2019).

Role of Extrusion in Starch Modification

Extrusion, a thermomechanical process, is a revolutionary technique known for its capability to disrupt the molecular bonds of starch, inducing starch gelatinization, melting, and degradation. This process induces significant structural and physicochemical alterations in starch, profoundly impacting its properties.



Structural Changes of Starch following Extrusion

Extrusion leads to notable modifications in the crystalline structure, granule morphology, and molecular arrangement of starch. For instance, native corn starch granules, when subjected to extrusion, undergo a drastic transformation. Initially polygonal and relatively smooth, the granules become irregular and rough due to the combined effects of high temperature and shear forces (Wang et al., 2021). This transformation results from the thermal effects and shear forces, leading to a fragmented, disrupted structure (Wang, Shogren, & Willett, 1997).

Physicochemical Properties of Starch following Extrusion

1. Expansion Ratio: The extrusion process causes starch to expand significantly, leading to a noticeable increase in volume.

2. Water Absorption Index and Water Solubility Index: Extrusion alters starch's water absorption and solubility characteristics. Extruded corn starch exhibits increased water absorption due to gelatinization reactions during extrusion (Wang et al., 2021).

3. Texture: Starch undergoes gelatinization, melting, and degradation during extrusion, resulting in changes in texture parameters such as hardness, cohesiveness, and springiness.

4. Pasting Properties: The pasting properties of starch are modified by extrusion, influencing characteristics like viscosity and gelatinization temperature.

5. Digestibility of Starch: Extrusion affects the digestibility of starch, influencing its nutritional properties. Amylopectin, a major component of starch, undergoes alterations during extrusion, leading to changes in the starch's digestibility (Garcia-Valle et al., 2021).

Conclusion

The extrusion process has revolutionized starch modification by inducing significant structural and physicochemical alterations in starch, profoundly impacting its properties. When subjected to extrusion, native corn starch granules undergo drastic transformations, becoming irregular and rough due to high temperatures and shear forces. These alterations include changes in crystalline structure, granule morphology, and molecular arrangement. Extrusion expands starch significantly, increasing its volume and altering water absorption and solubility characteristics. Additionally, extrusion affects texture parameters such as hardness, cohesiveness, and springiness, as well as pasting properties like viscosity and gelatinization temperature. Importantly, it influences the digestibility of starch, impacting its nutritional properties. Gelatinization, a pivotal step in extrusion, involves the irreversible destruction of the crystalline order within starch granules, significantly increasing water absorption and denoting enhanced gelatinization. The process also induces starch degradation, facilitating interactions with other components and offering advantages such as versatility in processing, low-cost requirements, production of high-quality products, energy efficiency, and environmental friendliness. These modifications enhance starch's functionality, making it a cornerstone biomaterial in various industries, ensuring its continued importance in a rapidly evolving world.

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Table 1 Characteristics of Cereal and Pulses Starches

Cereal	Starch Content (%)	Amylose Content (%)	Granule Shapes	Granule Size (µm)	Crystalline Pattern
Corn	~75	~25 (variable)	Spherical to Irregular	<1 to >100	A-type (Normal, Waxy) B-type (High-amylose)
Wheat	60-75	Varies (5-40)	Lenticular A-granules, Round B-granules	2-38	A-type (Normal, Waxy) B1-type (High-amylose)
Rye	22-25	~24.6-48.7	Large (A-type), Small (B-type)	23-40 (A-type), <10 (B-type)	A-type
Barley	75-80	23.1-30.0	Disc-shaped (A-type), Spherical (B-type)	-	-
Oat	~60	25.2-29.4	Irregular to Polygonal	7.0-7.8	A-type
Rice	>80	Varies (2-5 to 5-6)	Round, Angular, Polygonal	3-10	A-type (Short A chains)
Lentil	~50	17-52	Round or spherical, oval, or irregular shapes		C-type (CC-type, CA-type, or CB-type polymorphs)
Bean		17-52	*-do-*		*-do-*
Pea		48.8-49.6%	*-do-*		*-do-*

(Source: Wang *et al.*, 2022; Wang & Guo, 2020; Waterschoot *et al.*, 2015; Ashogban *et al.*, 2014)

Table 2 Characteristics and Uses of Horticultural Crops Starches

Crops	Starch Content (%) (d.w.)	Amylose Content (%)	Granule Size Range	Crystalline Pattern	Main Uses
Potato	66-80	25.2- 29.1	5 - 100 µm	B-type	Food processing, thickening agent, pharmaceutical filler
Cassava	70	25.2- 29.1	5 - 100 µm	B-type	Food processing, thickening agent, pharmaceutical filler
Yam	60-80	1.4- 50	1 - 90 µm	B- or C-type	Food products, cultural dishes
Sweet Potato	50-80	38	2 - 12 µm	A-type, C-type	Limited industrial applications, potential for growth
Winter Squash	65	-	-	C-type	Extensive study for post-harvest storage technology.
Tomato	20	-	-	C-type	Important site for starch storage; different starch features in columella and pericarp.
Apple	44-53.2	40-48	2-12 µm	CA-type	Starch increases during maturation; used in various cultivars.
Banana	69-82	15-23	-	A-, B-, or C-type	Highly resistant to enzymatic hydrolysis; potential for various applications.
Fritillaria	80	18.8-30.2	5-50 µm	B-type	Traditional Chinese medicine; mainly oval granules with various sizes.
Chinese Yam	20-60	10-23	5-60 µm	C-type (B-type in center, A-type at periphery)	Important invigorant in traditional Chinese medicine; decreases cholesterol levels in rats.

(Sources: Wang & Guo, 2020; Kumar *et al.,* 2019; Moorthy *et al.,* 2015; Chung *et al.,* 2014; Rollandsabaté *et al.,* 2012; Huang *et al.,* 2012)

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