MORPHOLOGICAL AND THERMAL PROPERTIES OF MAIZE STARCH

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Abstract
Maize, rice, wheat and potato are the main sources of starches which differ significantly in composition, morphology, thermal, rheological and retrogradation properties. Starch has unique thermal properties and functionality that have permitted its wide use in food products and industrial applications.
The structure of the starch granule results from the physical arrangement of amylose and amylopectin. Amylose content of starches from different maize types ranged between 15.3% and 25.1%. Amylopectin is considered responsible for the crystalline structure of starch granules.
The morphological and physicochemical characteristics of maize starch are related to the enzymes involved in its biosynthesis.
The surface of the starch granule plays a fundamental rôle as the first barrier to processes such as granule hydration, enzyme attack, and chemical reaction with modifying agents. Major parameters describing the solid surface are: specific surface area, total pore volume, mean pore radius (diameter) and pore volume distribution in relation to pore radius (diameter).

Keywords: swelling power, specific surface area, gelatinization

1. INTRODUCTON

Nature has chosen the starch granule as an almost universal form for packaging and storing carbohydrate in green plants [1]. Maize starch is one of the cereals of worldwide importance; this grain is used for human consumption and also has important industrial applications [2].
Corn starch granule polyhedral shape and diameter is between 5 and 25μm [24]. Granule shapes include nearly perfect spheres and discs, and polyhedral or irregular granules [1]. The granule size is correlated with some physicochemical and functional properties of the starch molecule: temperature and enthalpy, gelatinization, pasting characteristics, enzymatic susceptibility, swelling, and solubility [2].
As starch molecule is composed of an amorphous region (amylose) and crystalline region (amylopectin). Starch granules are partially crystalline, with crystallinity generally in the range of 15 to 45% [8]. Starch has two different crystalline structures (A and B) resulting from the association of double helices formed mainly by external amylopectin chains [11]. Proportion of amylose and amylopectin are from 20% to 25% for amylose and from 75% to 80% for amylopectin. When heated, in the presence of excess water, starch granules lose their crystallinity, absorb large amounts of water, and leach out amylose, which impart viscosity to the starch/water system [8].
Due to its complexity starch exhibits certain unique properties which are not encountered in other polysaccharides and which significantly affect its functionality (granule swelling, gelatinization, occurred when starch granules are heated at elevated temperatures in the presence of excess water, ability to interact with a number of linear polar and non polar molecules such as fatty alcohols, fatty acids, monoglycerides and others to form inclusion complexes) [9].
The characterization of the enzymes that are involved in starch biosynthesis has increased, these enzymes are responsible of the granule starch formation which influences molecular and structural characteristics and consequently the physicochemical and functional properties of starchy products [2]. However, only few enzymes such as granule-bound starch synthase (GBSS) and soluble starch synthase (SSS), which both produce the linear chains of alpha-1-4 glucosyl units, are responsible for the

biosynthesis of amylase and amylopectin, respectively [2]. Granule-bound starch synthase I (GBSSI) is one of the key enzymes catalyzing the formation of amylose, a linear alpha (1,4)D-glucan polymer, from ADP-glucose [4].

2. CHEMICAL COMPOSITION

Chemical composition of starch, before and after extracting protein obtained from white maize, is presented in Table 1 [2].

Table 1 Chemical composition of starch isolated from white maize starch

Content	White Maize
Protein [a]	7,5 ± 0,0b
Lipid	0,5 ± 0,1a
Ash	0,6 ± 0,0b
Apparent amylose	26,3 ± 0,2b
Total starch	78,7 ± 1,8b
Damaged starch	4,2 ± 0,2a
Protein[b]	2,5 ±0,0b
Total starch[b]	93,8 ± 1,0a
Damaged starch	5,1 ± 0,2b

[a] Nx6,25
[b] After protein extraction

The functional properties of starch are also influenced by the content of phosphate, i.e. a non-carbon component of starch. A distinction is made between phosphate which is covalently bonded in the form of monoesters to the glucose molecules of the starch and phosphate in the form of phospholipids which are associated with the starch.
The content of starch phosphate varies in dependence on the plant type. Thus, for example, certain corn mutants synthesize a starch having an elevated content of starch phosphate (waxy corn 0.002% and high-amylose corn 0.013%) whereas conventional corn types only exhibit traces of starch phosphate [17].

3. MORPHOLOGY

The morphology and topography of surface is an important feature of solids used as raw material [12].

Fig. 1 shows the granular structure of the maize starches observed by microscopy with different light sources. It is seen a mixture of rounded granules and angular granules [1].

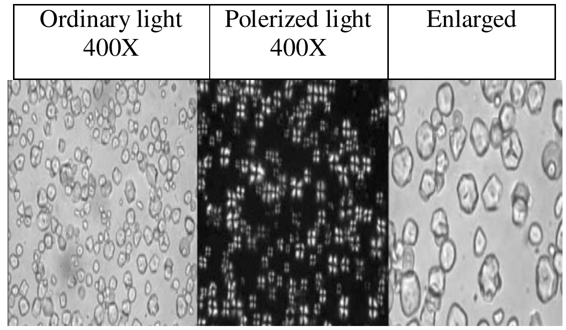

Fig. 1. Granular structure of maize starches observed under a light microscope with/without polarized light.

Scanning electron micrographs of the shape and surface details of the starch granules are shown in Fig. 2 [1].

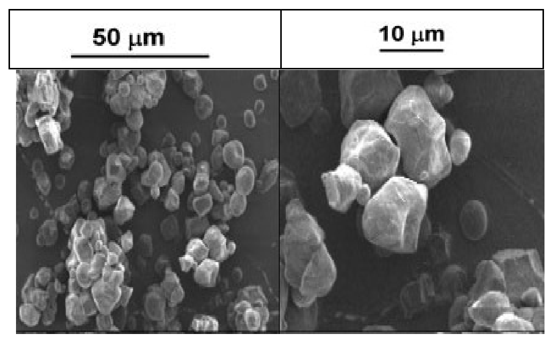

Fig. 2. Starch granules observed by scanning electron microscopy (SEM)

The morphology of starch granules depends on the biochemistry of the chloroplast or amyloplast, as well as physiology of the plant [14]. (Chloroplasts are organelles found in plant cells that conduct photosynthesis. Chloroplasts capture light energy to conserve free energy in the form of ATP and reduce NADP to NADPH through a complex set of processes called photosynthesis. Amyloplasts also convert this starch back into sugar when the plant needs energy). Amyloplasts are non-pigmented organelles found in some plant cells. They are responsible for the synthesis and storage of starch granules, through the polymerization of glucose [19].

4. SWELLING POWER OF MAIZE STARCH

By heating a water suspension of starch granule minor changes occur reversibly swells up when it reaches the critical temperature of starch gelatinization occurs. The swelling power is directly correlated to the increase in temperature. Swelling power of corn starch increased from 10% to 20% at 75^0C to 95^0C [22]. The molecular arrangement, which depends on the present amount of amylose and amylopectin, allows an estimation of the kind of organization occurring in the interior of the granule [8]. Maize starch granules have no internal structure favorable for water retention, that is characteristic of a low-starch amylopectin [22]. Swelling capacity of starch is positively influenced by the degree of mechanical damage of starch granules.
Corn starch is one which is stable under acidic conditions and sterilization [20].
K. Adedowale [23], shows increased swelling ability of starch in alkaline pH areas, this behavior by putting it on account of interaction between protein and starch in the alkaline zone, when both substances have a negative electrical charge, and interaction between them is weak. The acidic proteins are positively charged, their association is strong. Thus swelling capacity increases and decreases in alkaline regions in acidic pH regions, depending on the amount of protein associated with starch.

5. SURFACE OF STARCH GRANULES

The surface of the starch granule plays a fundamental rôle as the first barrier to processes such as granule hydration, enzyme attack, and chemical reaction with modifying agents. The nature of the surface, the presence of proteins and lipids, has many significant effects on starch properties. For example, the presence of lipid granules on the surface has a significant influence on the rheological properties of starch pastes water.
Starch granule associated protein and lipid are by far the most abundant of the minor components of starch . These components are naturally occurring; they are thought to be incorporated in the granule during its synthesis.
Starch processing involves many interfacial changes, the rate and efficiency of them is controlled mainly by surface structure of starch granules [12].
Major parameters describing the solid surface are: specific surface area, total pore volume, mean pore radius (diameter) and pore volume distribution in relation to pore radius (diameter) [6].
Was observed that the number of pores or fractures found on the surface of starch granules depends on moisture content and drying method [12].
Starches of corn, sorghum, millet, large granules of wheat, rye and barley observed by scanning electron microscopy (SEM) were found to have pores. However, it appears that some granules contain many pores, others a few, and some none on the surface observed. Moreover, all these experiments do not take into account the propensity of the granule to swell when water is absorbed, inducing higher porosity inside the amorphous matrix by inducing higher molecular mobility (plasticizing role of water). In fact, starch granules, as it has been demonstrated for gels, can be considered as porous material exhibiting both external and internal surface area. The external surface area is determined by the shape and size of the particle. The internal surface area is defined by the capillary structure of the hydrated particle [5].
Surface pores of corn starch can form centres of enzymatic attack [12]. If the surface is without fractures, cracks and pores the degree of erosion caused by enzyme is very low [12].
Open pores can be divided into those open at one or both ends. Because of their shapes, pores can be divided into cylindrical, conical and bottle-shaped ones [6].
Mesopores and macropores exist on the surface of starch granules whose specific surface areas are rather small (see Table 1) [6].

Table 2. Specific surface area (SBET), volume of mesopores and average diameter of mesopores for investigated starches

Type of starch	Specific surface area [m^2/g]	Volume of mesopores (cm^3/g)x10^{-3}	Avaraje diameter of mesopores (nm)
Maize	0,687 (0,0015)	1,10	6,42
Wheat	0,534 (0,002)	0,76	5,70
Triticale	0,383 (0,002)	0,68	7,07
Rice	1,267 (0,006)	1,95	6,76

Standard deviations are shown in brackets

6. MAIZE STARCH GELATINIZATION

Native starch granules, as appear in raw foods, are mostly indigestible. Gelatinization of starch occurs when foods are heated in an excess of water. During the gelatinization process, starch granules swell and gradually lose their molecular order; the amylose chains solubilize and a starch gel is formed. At this point, starch is easily digestible. Upon cooling, the gel undergoes transformations leading to a partially crystalline structure, both amylose and amylopectin taking part in this process that results in the formation of retrograded starch [13].

Gelation occurs in a starch paste when hydrated starch molecules that have dispersed due to heating begin to retrograde, a process of alignment and reassociation. Linear amylose molecules associate more readily through hydrogen bonding than the highly branched amylopectin molecules. At sufficiently high starch concentrations, the retrogradation of the amylose molecules forms a three-dimensional network that entraps water and creates a gel. Starches with greater amylase content form gels with greater strength [10].

Heat-gelatinization is a phase transition of granules from an ordered state to a disordered one during heating in excess water [8].

However, it was postulated that the gelatinization enthalpy depends on granule size and amylose: amylopectin relationship, apart from microstructure and crystallinity degree (quality and amount of crystals) of amylopectin. Studies with maize, rice and potato starches showed that the gelatinization enthalpy increased when chain length increased, but is important to consider the number of chains per cluster in the amylopectin molecule [3].

During the cooling phase, the starch undergoes retrogradation in which the starch chains begin to reassociate in an ordered structure, and this is accompanied by another rise in viscosity, usually referred to as setback.[15].

Retrogradation is a complex process in which amylose chains, solubilized during gelatinization, aggregate, forming crystalline double helices stabilised by hydrogen bonds. Upon cooling and ageing, these helices aggregate to form three-dimen-sional crystalline structures of the B-type. These crystallites are highly stable, showing a melting endotherm at about 150^{0}C, and are resistant to enzyme digestion. Amylopectin molecules can also crystallise by association of the short lateral chains. Whilst amylose etrogradation is a rather fast process taking place in few hours, amylopectin requires longer times (days or weeks). Amylopectin crystallites are less stable than amylose ones, with a melting point close to 60^{0}C. Therefore, storage conditions (time and also temperature of storage) are important factors in the retrogradation process [13].

Factors affecting maize starch gelatinization

Influence of pH on starch gelatinization

➢ Alonso-Garcia (1999) [13] studied the influence of pH on starch gelatinization concluded that the pH only affects the gelatinization of starch gelatinization of corn starch while from other sources is not influenced by pH variation. Corn gel values obtained at pH between 7 and 10 is more resistant than corn gel obtained from an acidic pH .

➢ Amani G.N. 2005 [20] studied the gelatinization of starch, derived from various sources, at pH 7 and pH 3, noted that all the starch gels are sensitive to acidic pH and viscosity solutions is on average lower than 31% from pH 7 to pH 3. Acids producing hydrogen bonds break relegation gels. Corn starch gel is more resistant to acid medium, low viscosity is only 19%.

Ratio amylose/ amylopectin

The amount of amylose from the granule affects the swelling capacity and gel strength. Starch gel is a solid-liquid system having a continuous network of liquid trapped inside the network. Increasing the amount of amylose from the granule leading to reduced swelling of the pellet, but the gel strength increases as the free amylose molecules form hydrogen bonds with amylopectin granules which hinders swelling and leads to the formation of a compact network, continuous [21].

Increasing amylose content results in some opaque gels, while gels obtained from a waxy starch rich in amylopectin, have a high content of clarity [20].

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