

INDUSTRIAL APPLICATIONS OF STARCH

Most of the starch produced in the world is used as food, but about one-third of the total production is employed for a variety of industrial purposes that take advantage of starch's unique properties. The ability to induce starch accumulation in plant organs unable to synthesize it, or to increase starch content at will, would be of great nutritional importance, and some progress has already been made in this respect (see the chapter, "Regulation of the Starch Synthesis Pathway: Targets for Biotechnology"). But quality is as important as quantity. The properties of starch isolated from different sources (e.g., the size of the granules, viscosity, degree of branching, gelation properties) vary greatly and affect the digestibility of the starch and its use in food and nonfood products. Much could be gained by manipulating starch quality—for example, by modifying the ratio of amylose to amylopectin. So far this has been achieved to some extent and in some species by genetic improvement, but in the not-too-distant future, it could be better achieved using recombinant DNA and molecular biology techniques.

It is important for the scientist who works with the basics of carbohydrate metabolism to know how the raw material is used by the industry, and for this reason, here we comment briefly on the use and manipulation of starch in the industrial setting.

I. INDUSTRIAL APPLICATIONS OF STARCH

Estimates (Rabinowitch, 1945) of the total amount of carbon fixed in photosynthesis by land plants is on the order of 2×10^{10} tons per year. Three grain crops (wheat, rice, and maize) and three tuber crops (potato, yam, and cassava) provide $\frac{4}{5}$ of the world's food calculated as calories. The amount of starch produced by the edible portions of these crops in one year exceeds 7×10^8 tons, of which about 6×10^8 tons are contributed by cereal grains.

Most of the starch used in the food and beverage industries is in the form of starch hydrolysates (e.g., glucose, maltose, and isoglucose syrups). In syrup production, yield, ease of processing, color, and flavor are the

factors that determine the choice of the raw material. The main application for nonhydrolyzed starch is as a thickener, and for this use the rheologic characteristics of starch pastes are important. These characteristics depend on the botanical source of the starch and include temperature of gelatinization, whether on gelatinization they produce a gel or a sol, whether the gel is opaque or clear, and the gel thickness.

About one-third of the total starch production is used for a variety of industrial purposes that take advantage of its properties (e.g., sizing of paper and board; adhesive in the paper, packaging, and textile industries). In the chemical industry, starch is used as a starting material in fermentative processes to produce polyols, acids, amino acids, cyclodextrins, and fructose.

II. MANUFACTURE AND PROPERTIES OF STARCH

Different processes are used in the manufacture of starch, depending on the plant source, but they all essentially involve freeing the starch granules from the other constituents (e.g., fiber, germ, proteins). Purification is usually done by screening, washing, and centrifugal separation, and the starch obtained is then dried. In the case of maize starch, mechanical separation is facilitated by steeping the grain in warm water in the presence of sulfite. Further processing of starch is carried out on starch suspensions because native starch is insoluble in water.

Little is known about the molecular bases for the differences in the behavior of starches from different sources, but some important factors are the proportion of amylose and amylopectin, the size of the amylose and amylopectin molecules, and the presence of phosphate ester groups (as in potato amylopectin). Potato starch has some favorable characteristics (e.g., its high water retention, slow retrogradation, formation of clear pastes, and lack of a distinctive flavor). Starch from a particular source may have shortcomings that make it inappropriate for a particular use: lack of free flow or water repellency, insolubility or failure to swell and develop viscosity in cold water, excess of viscosity after cooking, cohesive or rubbery texture of cooked starch, tendency to break down during extensive cooking, shear at low pH, lack of clarity, or tendency to become opaque and gel when cooked. The solution in these cases is either to change the source of the raw material or to modify the starch by chemical or physical methods. In maize, sorghum, rice, and barley, *waxy* mutants that have starches essentially free of amylose have been discovered. Starches with high levels of amylose are also known, and some lines of corn have been developed in genetic programs (starting with Whistler and Kramer in the 1940s) with

starch containing up to 70% amylose (the normal is around 25%); such cereals are called *amylotypes*.

Viscosity and "mouth-feel" of gravies and other prepared foods, and the behavior of baked products, are determined primarily by the behavior of the starch present in those foods. Starch is responsible for the viscosity and mouth-feel of gravies and puddings and the texture of gumdrops and pie fillings. Baking products "set"—that is, there is a temperature at which the dough no longer expands under the gas pressure generated by the increasing temperature—and the changes experienced by the starch in the dough are responsible to a great degree for that setting. Thus, a great deal of attention has been devoted to the behavior of starch in water. Dried starch granules swell when they are suspended in water; starch can hold up to approximately 30% of its dry weight in moisture. If the temperature is increased slowly, the granules continue to expand slowly. At that stage, they still maintain their crystalline and birefringent properties, and the temperature-induced swelling is still reversible. However, if the temperature is further increased, irreversible swelling occurs, and the granules lose their birefringence. This phenomenon, called *gelatinization* occurs over a range of 5 to 10°C and can be tracked in a number of ways. The optical properties can be examined using a microscope equipped with a hot stage. As temperature is increased, viscosity can be followed using an amylograph (Fig. 1), and as the swelling progresses, so does viscosity, which is measured in Brabender units. Then, as temperature is increased further, the swollen granule breaks down, causing a decrease in viscosity. Starch gelatinization is defined as the loss of birefringence, and this change coincides with a large increase in viscosity. An amylograph measures the relative viscosity of a system as it is heated at a constant rate (1.5°C/min). With continued heating, the starch granule becomes distorted, and soluble starch is released into the solution. The viscosity changes shown by the starch as temperature increases after gelatinization (i.e., after the loss of birefringence) are called *pasting behavior* and vary with the source of the starch and with the amylose content. Heating in the amylograph is stopped at 95°C, the temperature is left constant at that value for some time, and the starch is said to be cooked. During "cooking," the viscosity drops if the system is stirred, because the starch molecules orient themselves in the direction of stirring, a phenomenon called "shear thinning." Another property varies with the source of the starch: The more soluble the starch, the more it "thins" (the more the viscosity drops) on stirring. After the period of time at constant temperature, cooling of the system leads to a rapid increase in viscosity, the "setback," which increases as the hydrogen bonding between the starch molecules increases. This paste

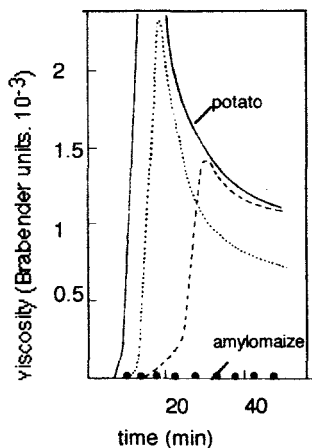


FIG. 1. Pasting behavior of different starches as measured using a Brabender amylograph. Viscosity is measured at varying temperatures; a standard program starts at 50°C, then heats at 1.5°C/min until a temperature of 95°C is reached, and then the temperature is kept constant at 95°C for 30 min. The sources of the different starches is as follows: —, potato; ·····, waxy maize; - - -, maize; ● ● ●, amylo maize. The first rise in viscosity is linked to the initial swelling of the starch granule, and is followed by a breakdown of swollen granules and a consequent decrease in viscosity. On gelatinization, potato starch swells greatly and then bursts open; cereal starches swell, but tend not to burst, and amylo maize starch swells very little. After Banks and Muir (1980).

is a gel holding large quantities of water. As the paste is cooled, the interactions increase and the gel becomes firmer. If the gel is frozen and thawed, or when it ages, interactions among the starch molecules increase and those with the water decrease, resulting in the loss of water by the gel, which is a phenomenon called *syneresis*. Longer storage leads to even stronger interaction among the starch molecules and eventually to the formation of crystals, a process called *retrogradation*. Crystallization changes the refractive index and the aged gel is more opaque, rigid, and rubbery. Retrogradation is thought to be responsible, at least in part, for the staling of bread, the setback of starch gels, and the skinning of pastes. Waxy starches do not retrograde.

The heat of gelatinization, which can be measured using differential scanning calorimetry, seems to be related directly to the amylopectin content, indicating that amylopectin (and not amylose) is the component responsible for the crystalline structure of starch (see the chapter, "Physico-chemical Structure of the Starch Granule").

III. PHYSICAL ANALYSIS OF STARCH AND DERIVATIVES IN THE INDUSTRIAL SETTING

X-ray analysis can be used to differentiate between native starches or to detect changes brought about by physical or chemical treatment of granular starch. Cereal starches give the A pattern, with the exception of amylomaizes, which have an amylose content greater than 40 or 45%. Starch precipitated from pastes by evaporation exhibit different patterns depending on the temperature of evaporation, B if below 50°C, B or C if above 50°C.

Light microscopy supplies information on the dimensions and shape of the granule, and helps to identify the botanical source of the starch and to monitor processing conditions and modifications. The progress of gelatinization can be followed using a polarizing microscope to observe the disappearance of birefringence using a Kofler hot stage, or by using Congo red, which stains gelatinized or broken granules but not native ones. Iodine staining is used to determine the degree of contamination of waxy starch (which stains red) with normal blue-staining granules. Granule size range and diameters can also be measured using a Coulter particle size counter.

The Brabender amylograph is a rotational instrument that permits the measurement of viscosity while cooking and cooling the starch paste. An aqueous dispersion of starch (10% w/w dry basis) is heated to 95°C at a rate of 1.5°C/min. Viscosity is recorded continuously during heating to give the hot-paste viscosity measurements. The peak viscosity indicates the highest viscosity that the industrial user will encounter on preparing a usable paste. The viscosity on reaching 95°C, relative to the peak viscosity, reflects the ease of cooking the starch. After cooking the paste for some time (e.g., 1 hour), the viscosity indicates the stability or degree of breakdown of the paste. Samples in the Brabender amylograph can later be cooled to approximately 50°C for the assessment of the "setback" characteristics (i.e., increased viscosity on cooling). The gels can also be prepared using a viscometer; the gels are cast in molds and, after storage at 20°C for 24 hours, the gel strength is measured as the energy required to compress the gel and the resistance of the gels to rupture.

Polarimetry takes advantage of the high specific rotation of starch, about +200, and is used mainly to measure concentration. It is affected by molecular structure, solvent, and hydrolytic degradation.

Differential scanning calorimetry measures heat flow as a function of temperature. When starch is heated in the presence of excess water, a sharp peak (an endotherm) is obtained, which is caused by the disordering of

amylopectin during the gelatinization. The starches that contain lipid give a second endotherm due to the dissociation of an amylose-lipid complex.

IV. CHEMICAL MODIFICATION OF STARCH

Lintner and Naegeli used acid treatment of starch in the late 1800s and, for this reason, acid-treated starches are called *lintnerized* or *Naegeli starches*. In this method, a concentrated starch slurry is heated in 1 to 3% HCl at about 50°C for 12–14 hours, leading to partial acid hydrolysis of the glucosidic bonds in the amorphous portion of the starch. The crystalline areas are not freely accessible to the acid and remain intact. After neutralization and recovery by filtration, the modified starch, with a lower molecular weight but with its crystalline structure intact, displays different characteristics on heating it in water. The granules fragment more and swell less, and the temperature range of gelatinization increases and, on gelatinization, the starch becomes soluble. The resulting paste is less viscous and the gels are more rigid. Acid-modified starches are used in jelly beans and other gum confectioneries.

Crosslinking of starch molecules to make larger ones is performed by forming a diester with phosphoric acid or an ether bond with epichlorohydrin. In a large molecule such as amylopectin, crosslinking can also occur internally. A high degree of crosslinking increases the gelatinization temperature to such an extent that starch can be boiled in water or sterilized in an autoclave and will not gelatinize. A lower degree of crosslinking (which is measured by “degree of substitution”) does not affect gelatinization, but strongly affects pasting properties (e.g., viscosity on pasting is decreased and shear thinning decreases—viscosity is not decreased much by shear and pumping) and allows gelatinization in an acidic medium such as that of a cherry pie. Crosslinking slows retrogradation and decreases the changes suffered by the gel on freezing and thawing.

Starch molecules that are modified by forming monoesters of phosphoric acid repel one another because of the added charge, leading to higher swelling and solubilization during gelatinization, and to less interaction during pasting. The resulting starch paste has a higher viscosity, lower resistance to shear thinning, and lower retrogradation and opaqueness. Depending on the degree of substitution, gelatinization can even occur at room temperature, and these starches are useful in the making of instant puddings. Oxidized starches, obtained by treatment with hypochlorite, give better adhesion to meat products but are generally used for nonfood purposes such as the manufacture of paper.

Other useful modifications include acetylation, hydroxyethylation, hydroxypropylation, cationic starches, succinate, and substituted succinate derivatives of starch. In starch-grafted copolymers, free radicals are initiated on the starch that then act as macroinitiators for the acryl or vinyl monomers. These products are used in firefighting fluids, electrolyte solutions for alkaline batteries, wound dressing, and so on.

V. CONVERSION OF STARCH INTO SWEETENERS

In the industry, the degree of hydrolysis is measured as dextrose (glucose) equivalents, or DE, which is a measure of the reducing power of the mixture relative to the number of glucose residues. Simple acid hydrolysis of starch leads to the formation of glucose syrup, because both the α -1,4 and the α -1,6 bonds are susceptible to the acid. However, after a certain DE is obtained, side reactions can occur that can affect the quality of the syrup obtained. For this reason, acid treatment is often used for thinning (i.e., for partial hydrolysis rather than a total degradation). The resulting dextrans can be used directly for increasing the viscosity of a number of products, but for the production of sweeteners, they must be further degraded using enzymes such as α -amylase, β -amylase, and/or glucoamylase. If a very high degree of sweetness is desired, glucose can be converted into fructose by the action of glucose isomerase.

VI. BIODEGRADABLE POLYMERS

Starch and starch derivatives can improve the biodegradability of a polymer as a whole when incorporated as fillers or functional additives (Booma *et al.*, 1994). Although starch-based polymers have also been developed, research continues with the following aims: to increase the speed and degree of degradability, to increase compatibility with inks, to decrease toxicity and hygroscopy, and to improve mechanical and rheologic properties. High amylose starch can be processed by extrusion or injection molding under highly controlled environmental conditions to give biodegradable thermoplastic materials (Fanta and Doane, 1986; Booma *et al.*, 1994). All industrial applications require some modification of the starch (e.g., the addition of plasticizers, chemical bonding, addition of high cost ethylene-acrylic acid copolymers). Although a variety of starches are being used for the manufacture of biodegradable polymers, it is likely that starches from some plants may be more suitable than others for a particular purpose. Indeed, a number of specialty starches

(such as amylose and waxy starch) are being increasingly recognized for their specific properties and biodegradability, and there is certainly room for other novel products. Thus, a greater understanding of the critical components of the plant starch biosynthetic machinery could have a major impact on agriculture and industry.

FURTHER READINGS

These sources provide additional in-depth coverage of this topic. For complete reference, please see the Reference section at the end of the book.

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