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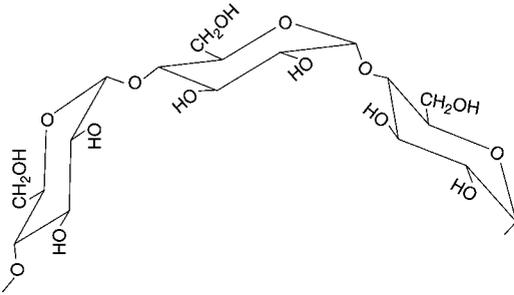
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## 1. Introduction

Starch [9005-25-8] is widely used in nonfood industrial applications, especially in the production of paper and paperboard products, as a textile sizing agent, and in fermentation processes to produce ethanol and other products, and in the processed food industry as a thickener/stabilizer, gelling agent, and a starting material for the production of sweeteners and polyols. It is also the principal source of dietary calories for the

world's human population. The chemistry and technology of starch has been reviewed in several books [1–7].

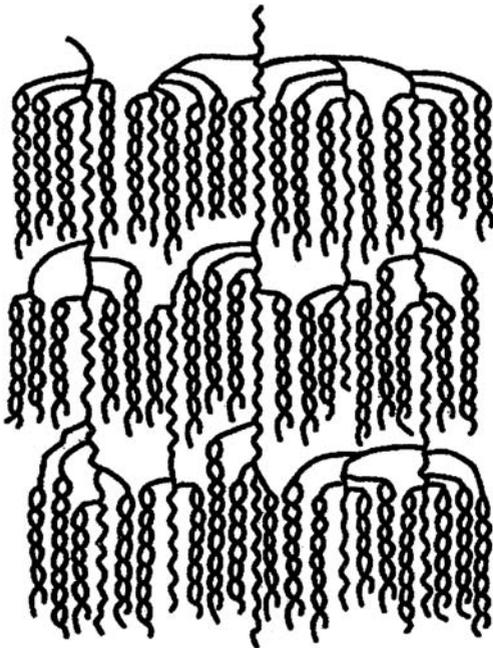
Native starch occurs as discrete particles called granules. A starch from a specific biological (plant) source is unique among starches, i.e., starch granules from the various plant sources differ in appearance, particle size distribution, fine structure of the constituent polymer molecules, and physical properties. Most applications of starch are realized only after the starch is



**Figure 1.** A three-glucosyl unit segment of an unbranched (i.e., linear) portion of an amylose or amylopectin molecule

heated (cooked) in the presence of water, a process that destroys its granular structure and releases its constituent polymer molecules.

Granular starch is generally composed of two types of molecules, amylose and amylopectin (Chap. 4). *Amylose* [9005-82-7] is a predominantly linear (1,4)- $\alpha$ -D-glucan (Fig. 1), although some amylose molecules are slightly branched. *Amylopectin* [9037-22-3] (Fig. 2) has a branch-on-branch structure consisting of mostly short



**Figure 2.** A representation of amylopectin molecules showing crystalline packing of double-helical pairs of branch chains  
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chains of (1,4)-linked  $\alpha$ -D-glucopyranosyl units (sometimes referred to as anhydroglucose units) linked to other short, linear chains via  $\alpha$ -(1,6) branch points. The amylopectin fraction is composed of much larger molecules than those of amylose. Most normal starches contain 70–75% amylopectin molecules by weight. Different molecular structures and sizes, amylose/amylopectin ratios, and granular architectures give each type of starch its unique properties.

## 2. Sources of Commercial Starches

Major crops used for starch production include corn (maize), cassava, potato, and wheat. Corn used to produce starch includes hybridized genetic variants of corn (Chap. 4). Lesser amounts of starch are isolated industrially from arrowroot, mung bean, rice, sago palm, sweet potato, yam, yellow pea, and other plants.

## 3. Worldwide Starch Production

In 2006, it was reported that 99% of the global starch production of ca.  $60 \times 10^6$  t originated from crops of corn/maize, cassava/tapioca, wheat and potatoes, with 73% being maize starch, 14% tapioca starch, 8.1% wheat starch, and 3.7% potato starch [8]. Starch is predominantly produced in the USA, the EU, Japan, and Thailand. The largest commercial starch producers worldwide are Cargill ( $9.2 \times 10^6$  t, 14.6%), CPI ( $5.2 \times 10^6$  t, 8.2%), ADM ( $5.2 \times 10^6$  t, 8.2%), National Starch and Chemical Co. ( $1.2 \times 10^6$  t, 1.9%), and Avebe ( $0.6 \times 10^6$  t, 1.0%). Approximately  $33.6 \times 10^6$  t (53.1%) of starch is produced by small to medium-sized companies.

### 3.1. Starch Production and Consumption in the EU

The starch industry in Western Europe is comprised of 24 different companies with 68 plants, which in 2005, produced  $9.6 \times 10^6$  t of starch distributed as follows: 46% corn/maize starch ( $4.4 \times 10^6$  t), 36% wheat starch ( $3.4 \times 10^6$  t), and 18% potato starch ( $1.7 \times 10^6$  t) [8]. Production of starch from yellow pea has also been instituted.

In 2005,  $9.0 \times 10^6$  t of starch products were consumed in the EU for production of starch hydrolysates, including high-fructose syrups ( $5.1 \times 10^6$  t, 57%), native starches ( $2.1 \times 10^6$  t, 23%), and modified starches ( $1.8 \times 10^6$  t, 20%). Approx. 57% of the  $9.0 \times 10^6$  t was used in the processed food industry and 43% in the nonfood sector. The breakdown by application areas/market sectors was as follows: sweets and drinks (confectionary, beverages, fruit processing) 30%, processed food (convenience food, bakery, food ingredients and food preparations, dairy products and ice cream) 27%, paper and corrugated board manufacture 28%, chemical, fermentation, and other industrial products 14% (Chap. 10).

### 3.2. The USA Corn Wet-Milling Industry

By far the majority of starch produced in the USA is isolated from corn/maize, with relatively small amounts of potato and wheat starch also being produced. Corn starch is produced by a wet-milling process (Section 8.1). Production figures for member companies of the Corn Refiner's Association (USA) for 2008 are given in Table 1 [9]. The production ratio of high-fructose syrups to glucose syrups was approx. 67:33. In addition,  $4.5 \times 10^9$  L of fuel ethanol [64-17-5] was produced by corn wet millers, although most of the fuel ethanol made in the USA by fermentation was obtained from corn by a dry-grind process. The sale of coproducts (see Table 1) from the wet-milling process is important to the economic viability of the industry.

**Table 1.** Products from the corn wet-milling industry in the United States for 2008

Product <sup>a</sup>	Production, $10^6$ t
Sweeteners <sup>b</sup>	5.2
Starches <sup>c</sup>	1.5
Coproducts <sup>d</sup>	5.9

<sup>a</sup> Dry weight.

<sup>b</sup> Also called conversion products. Includes high-fructose syrups (42% and 55% fructose), glucose syrups, crystalline glucose (dextrose), crystalline fructose, maltodextrins, and syrup solids.

<sup>c</sup> Includes native corn starches, modified corn starches, and dextrins.

<sup>d</sup> Includes corn oil, corn oil meal, corn gluten feed, corn gluten meal, and steepwater.

### 3.3. Tapioca Starch Production in Thailand

The greatest amount of tapioca starch is produced in Thailand. Lesser amounts are produced in Indonesia, Brazil, and China. In 2009, Thailand exported  $1.8 \times 10^6$  t of native tapioca starch,  $0.7 \times 10^6$  t of modified tapioca starch, and  $0.02 \times 10^6$  t of tapioca pearls (total =  $2.5 \times 10^6$  t) [10].

## 4. Molecular Structures and Properties of Amylose and Amylopectin

**Amylopectin.** The major polysaccharide of starch, amylopectin, is a very large, highly-branched molecule. The branch points constitute 4–5% of the total glycosidic linkages and occur in clusters. There are three general classes of chains. A chains are those that are connected to another chain via a (1, 6) linkage, but are themselves unbranched. B chains are those chains that are connected to another chain via a (1, 6) linkage and have one or more A chains or other B chains attached to them, i.e., they are further branched. B chains can be subdivided into chains of various lengths/sizes. The C chain is the one possessing the lone reducing end-unit of the amylopectin molecule. In starch granules, the A and short B chains occur as pairs of chains entwined around each other in double helices (Fig. 2), which pack together to give rise to the crystallinity of starch granules. Average molecular masses of amylopectin molecules are at least  $10^7$  and may be as large as  $10^9$ .

The original cluster model for amylopectin has been refined several times, but has kept its basic form [11–14] until recently when a variation was proposed [15] that accounts for the superhelical nature of the amylopectin molecules proposed to be present in at least some starches.

Amylopectin is present in all known starches, constituting about three-fourths of most normal starches (Tables 2 and 3); indeed, some starches consist entirely of amylopectin (i.e., they lack amylose). Starches containing only amylopectin (all-amylopectin starches) are often referred to as *waxy starches*. Average fine structures, average molecular masses, molecular mass ranges, and

**Table 2.** General properties of granules and pastes of native corn/maize starches

	Normal corn starch	Waxy maize starch	High-amylose corn starch <sup>a</sup>
Granule size, $\mu\text{m}$	2–30	2–30	2–24
Amylose (approx.) <sup>b</sup> , %	28	0	50–70
Gelatinization/pasting temperature <sup>c</sup> , °C	74–81	66–71	66–71 <sup>d</sup>
Relative viscosity	medium	medium-high	very low
Paste rheology (body)	short	long	short
Paste clarity	opaque	slightly cloudy	slightly opaque
Tendency to gel/retrograde	high	very low	very high
Gel consistency	firm	nongelling	very firm
Lipid, % ds <sup>e</sup>	0.8	0.2	–
Protein, % ds <sup>e</sup>	0.35	0.25	0.4
Starch-bound phosphorus, % ds <sup>e</sup>	0	0	0
X-ray diffraction pattern type	A	A	B

<sup>a</sup> Also known as amylo maize starch.

<sup>b</sup> The percentage of amylopectin is the difference between 100% and the percentage of amylose.

<sup>c</sup> From the initial temperature of gelatinization to complete cookout.

<sup>d</sup> Under ordinary cooking conditions, where the slurry is heated to 95–100 °C, high-amylose corn starch produces little viscosity.

Gelatinization of high-amylose corn/maize starch with ca. 50% apparent amylose content may begin as low as 66 °C and end as high as 166 °C, depending on the moisture content. Gelatinization of high-amylose corn/maize starch with ca. 70% apparent amylose content may begin as low as 66 °C and end as high as 171 °C, depending on the moisture content.

<sup>e</sup> ds = dry solids.

perhaps, the shapes of amylopectin molecules vary from starch to starch and are important determinants of the physical properties of a starch, as well as foods and/or other products that contain starch.

**Amylose**, the other naturally occurring starch biopolymer, is an essentially linear chain of (1,4)-linked  $\alpha$ -D-glucopyranosyl units (Fig. 1). Some amylose molecules are slightly branched, with branch points constituting 0.3–0.5% of the total glycosidic linkages. Because there are only a few branches, with the branches usually being either very long or very short chains, and because

the branch points are usually far apart, amylose molecules behave as linear polymer molecules. The average molecular masses of amyloses from different commercial starches are in the  $10^5$ – $10^6$  range, which means that they have average *degrees of polymerization* (*DP*, number of glucosyl units per molecule) of ca. 600–6000. The nature of the glycosidic linkages in amylose chains produces a natural right-handed helix (Fig. 1), which has consequences for its properties.

Most starches contain 25–30% amylose (as shown in Tables 2 and 3, where their general properties are outlined) and are known as normal starches. Starches containing more than this

**Table 3.** General properties of granules and pastes of potato, tapioca, and wheat starches

	Potato starch	Tapioca starch	Wheat starch
Granule size, $\mu\text{m}$	5–100	4–35	0.5–45 <sup>a</sup>
Amylose (approx.) <sup>b</sup> , %	21	17	28
Gelatinization/pasting temperature <sup>c</sup> , °C	58–65	52–65	52–85
Relative viscosity	very high	high	medium-low
Paste rheology (body)	very long	long	short
Paste clarity	clear	clear	cloudy
Tendency to gel/retrograde	medium-low	low	high
Gel consistency	salve-like	soft	soft
Lipid, (% ds) <sup>d</sup>	< 0.1	< 0.1	0.9
Protein, % ds <sup>d</sup>	0.1	0.1	0.4
Starch-bound phosphorus, % ds <sup>d</sup>	ca. 0.08	0	0
X-ray diffraction pattern type	B	A	A

<sup>a</sup> Bimodal population.

<sup>b</sup> The percentage of amylopectin is the difference between 100% and the percentage of amylose.

<sup>c</sup> From the initial temperature of gelatinization to complete cookout.

<sup>d</sup> ds = dry solids.

amount of amylose are known as *high-amylose starches*. Two commercial corn starches, known as high-amylose corn starches or *amylomaize starches*, have apparent amylose contents of ca. 50% and >70%.

Several particular properties of amylose are important with regard to applications of starch. Heating of starches in water with shear forms what are called *pastes*. Pastes from amylose-containing starches are generally opaque and usually form firm gels upon cooling. Precipitation, rather than gelation, may occur in dilute pastes as they cool. The opacity and the formation of a gel or a precipitate results from amylose molecules associating with each other in crystal-line order, a process that is called *retrogradation* (see Section 5.2.2), or when it is associated with determining paste properties, *setback* (see Section 5.2.3).

Helical amylose chains have hydrophobic interiors capable of forming inclusion complexes with linear hydrophobic portions of molecules that can fit within the lumen (i.e., the inner cavity) of the helix. When a hot, aqueous dispersion of starch is stirred with a slightly polar, slightly water-soluble organic compound, such as butan-1-ol, and then cooled, amylose complexes crystallize out and can be isolated by centrifugation. Complexation stabilizes the helix and converts the long, linear molecules into more uniform and more rod-like structures. Because only the amylose molecules crystallize, such complexation can be employed to isolate pure amylose.

Iodine (as  $I_3^-$ ) complexes with amylose and amylopectin molecules, with complex formation also occurring within the hydrophobic interiors of helical segments of starch molecules. The long helical segments of amylose allow long chains of poly( $I_3^-$ ) to form and produce the blue color that is a diagnostic test for starch (more specifically, amylose). The amylose–iodine complex contains 19% iodine, and determination of the amount of iodine complexed is used to measure the amount of apparent amylose in a starch. Amylopectin forms reddish brown complexes with iodine because its branches are too short for the formation of long chains of poly( $I_3^-$ ).

Polar lipids (surfactants/emulsifiers and fatty acids) affect starch pastes and starch-based foods in one or more of three ways as a result of complex formation: (1) by affecting starch gelatinization (see Section 5.2.1) and pasting, (2) by

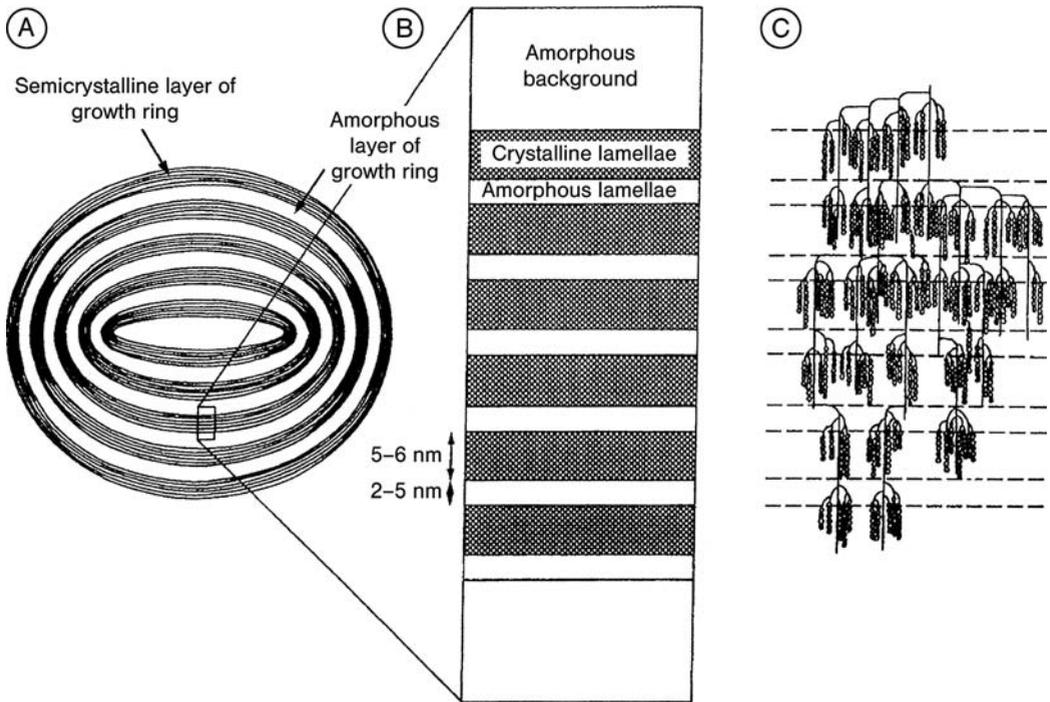
modifying the rheological behavior of the resulting paste, and (3) by inhibiting (or in some cases accelerating) the crystallization of starch molecules associated with the retrogradation process. Specific changes to a paste that are observed upon the addition of a lipid depend on its structure and the starch employed, i.e., different lipids/surfactants affect the gelatinization and pasting behaviors of a given starch differently, and each lipid/surfactant affects starches from different botanical sources differently. Because complex formation with emulsifiers occurs much more readily with amylose and, as a result, has a much greater effect on amylose molecules than on amylopectin molecules, polar lipids have a much greater effect on normal starches than on waxy (all-amylopectin) starches. Addition of most lipids/surfactants/emulsifiers to starches containing amylose inhibits the processes associated with gelatinization and pasting, but some speed up these processes and/or cause them to occur at lower temperatures. Polar lipids inherent to native cereal starches generally inhibit retrogradation.

The ability of polar lipids to form complexes with amylose and amylopectin is associated with their chain length, their degree of unsaturation, and the nature of their hydrophilic group. In general, esters of myristic ( $C_{14}$ , saturated) and palmitic ( $C_{16}$ , saturated) acids are most effective.

## 5. Structures and Properties of Starch Granules

### 5.1. Granule Structure

Within plants, synthesized starch molecules are assembled in the form of semicrystalline aggregates, termed granules, which vary according to size (< 1–100  $\mu\text{m}$ ) and shape (spherical, ellipsoidal, polygonal, lenticular, etc.) depending on their botanical origin [16]. Starch granule biosynthesis occurs within an organelle called the *amyloplast* and originates at a point called the *hilum* (the approximate center of the granule), from which site starch molecules are deposited in a radial, spherocrystalline arrangement [17]. The precise architecture of starch granules is rather complex and consists of multiple levels of structural organization. At the most basic



**Figure 3.** Schematic diagram of the starch granule

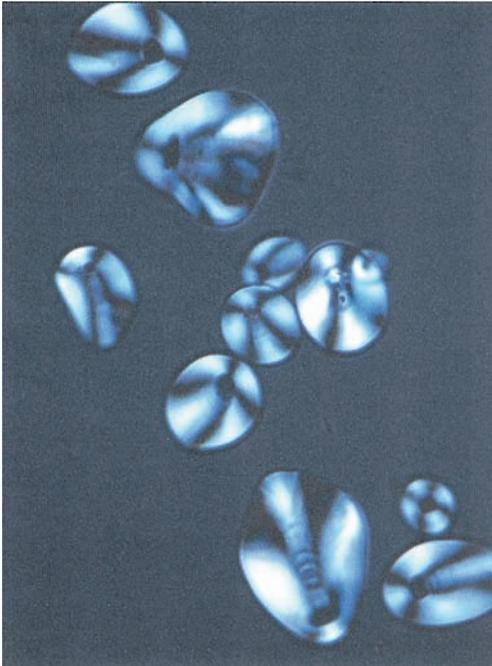
A) Structural relationship between the semicrystalline and amorphous shells (growth rings); B) Structural relationship between crystalline and amorphous lamellae; C) Amylopectin molecular structure

(Reprinted with permission from P.J. Jenkins, R.E. Cameron, A.M. Donald, W. Bras, G.E. Derbyshire, G.R. Mant, A.J. Ryan, *J. Polym. Sci., B-Polym. Phys.* **32** (1994) 1579.)

organizational level, the granule is comprised of alternating semicrystalline and less crystalline (frequently called amorphous) shells, commonly referred to as growth rings [17–19] (Fig. 3). On a higher organizational level, a semicrystalline shell or growth ring itself is comprised of alternating crystalline and amorphous lamellae, which correspond to the molecular features of amylopectin molecules. The branching regions of amylopectin molecules comprise amorphous areas within the crystalline regions of both shells, while the short, linear segments of amylopectin branch chains organized in double helices (Chap. 4) constitute the crystalline lamellae. Another level of organization, intermediate to those already described, involves aggregation of adjacent double-helical segments of amylopectin to form crystalline blockets [17, 18]. In short, amylopectin is primarily responsible for the organization of starch granules and accounts for their semicrystalline nature. In contrast, amylose is believed to be located in amorphous regions, where it is proposed to be randomly interspersed

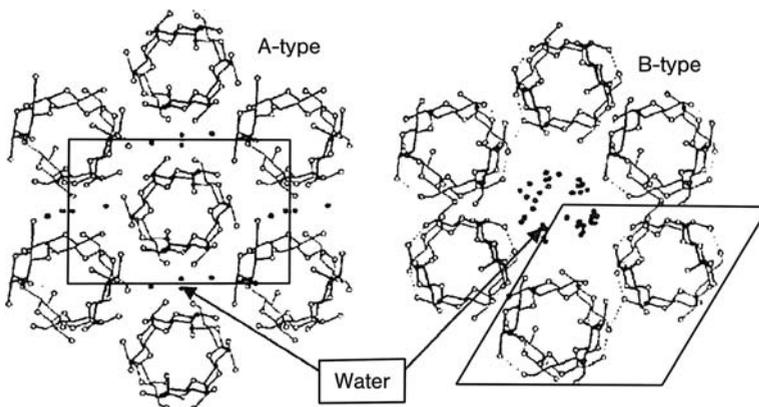
among amylopectin clusters and/or to be involved in complexes with native polar lipids [17].

The spherocrystalline radial arrangement of starch molecules in the granule is inferred from the birefringence (as evidenced by the Maltese cross) that is seen on microscopic examination of starch granules under plane-polarized light [17] (Fig. 4). As determined by X-ray diffraction, native starch granules generally exhibit crystallinities ranging from 15–45% [20, 21]. X-ray diffraction of native starches reveals three distinct patterns, A, B, and C (not to be confused with the A, B, and C chains of amylopectin molecules already described), which define the specific allomorphic packing arrangement of starch double helices (i.e., crystallites) present within granules (Fig. 5) [17, 20]. The specific type of crystallite packing observed in a starch is primarily a function of both the temperature condition within the plant during starch synthesis and the chain length. An average chain length in excess of DP 12 tend to favor the formation of the B allomorph over the A allomorph (average DP



**Figure 4.** Depiction of the Maltese cross observed within starch granules (potato) viewed under plane-polarized light

10–12) [17]. In general, tuber starches produce B crystallites (starch synthesized underground under cool conditions), while cereal starches possess an A crystalline arrangement (starch synthesized above ground under hot, dry conditions); legume starches exhibit the C allomorph, which is a mixture of A and B crystalline allomorphs [17, 20].



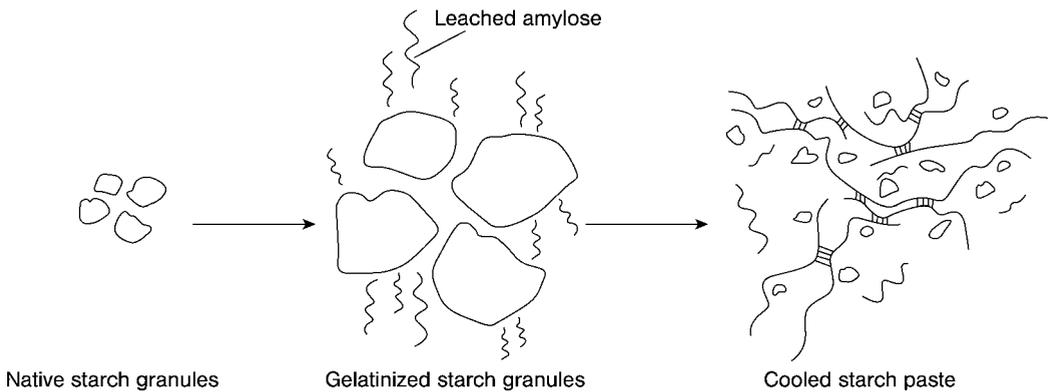
**Figure 5.** Depiction of A and B polymorphic structures for starch double helices (Reprinted with permission from H.F. Zobel, *Starch/Stärke* **40** (1988) 1.)

At the macrostructural level, granules of corn/maize and wheat starches possess pores on external granule surfaces [22–24], which features represent openings to channels leading into the granule interior [23–26]. Channels within granules of these starches have been demonstrated to impact granular patterns of amylolytic degradation and chemical modification by facilitating access of enzymes and chemical reagents to the granule interior [22, 27–29].

## 5.2. Physicochemical Properties

Native starch granules, which possess complex long-range and short-range molecular order, are insoluble in cold water, but are nevertheless capable of absorbing water (0.48–0.56 g/g dry starch) due to their semi-amorphous nature [30]. In hydrated granules, water has a plasticizing effect on amorphous regions, effectively lowering the overall glass transition temperature ( $T_g$ ) and enhancing mobility of the biopolymers. Hydration (at 25 °C) produces increases in granule diameter (i.e., swelling) of approximately 10% and 25% for normal and waxy corn starch, respectively, which swelling is reversible in nature.

The most significant physicochemical properties of starch are associated with irreversible thermal transitions that result in increased starch granule swelling and dissolution of the starch biopolymers. Heating of starch granules in excess water (i.e., water-starch ratios > 1.5:1) brings about *gelatinization* (the irreversible loss



**Figure 6.** Schematic representation of the structural changes associated with the gelatinization and pasting of native starch granules. Gelatinization (loss of granular molecular order) is accompanied by granule swelling and leaching of soluble starch components (amylose) during heating in an aqueous system. With the application of shear, swollen granules undergo further disintegration to yield a paste, which is comprised of a continuous phase of solubilized starch and a dispersed phase of granule remnants. Upon cooling, amylose retrogradation (depicted by the cross-hatching between molecules within the paste) results in the formation of a gel network. (Reprinted with permission from K.C. Huber, A. McDonald, J.N. BeMiller: "Carbohydrate Chemistry", in Y. H. Hui, F. Sherkat (eds.): *Handbook of Food Science, Technology, and Engineering*, vol. 1, Taylor & Francis/CRC Press, Boca Raton, 2006.)

of granular/molecular order), which is accompanied by increased granule hydration, swelling, and leaching of soluble components (primarily amylose) (Fig. 6) [31]. Upon heating, hydrated molecules within granule amorphous regions begin to vibrate, inducing progressive disruption of hydrogen bonds to further increase hydration and plasticization of starch molecules within granules. Granule swelling becomes irreversible as the strain imposed within granule amorphous regions becomes sufficient to bring about assisted disruption of starch crystallites. Gelatinization is marked by the disappearance of birefringence and a complete loss of granule crystallinity [30]. When starch is present in sufficient concentration (generally 2–7%), swollen granules begin to press against one another as they occupy nearly the entire volume of the aqueous continuous phase, leading to greatly increased viscosity.

In the presence of shear, highly swollen granules are fragile and disintegrate to form a *paste*, which is comprised of hollow, swollen granules (ghosts) and broken granule remnants (ghost fragments) dispersed within a continuous phase of partially dissolved starch molecules. As a paste is cooled, amylose molecules reassociate or recrystallize in a process called *retrogradation*, which involves formation of double-helical structures that aggregate to form a three-dimensional gel network (Fig. 6) or pre-

cipitate [32]. Starch gels are a two-phase, mixed gel comprised of both amylose-rich and amylopectin-rich regions due to incompatibility of the two polymers [31]. Due to their branch-on-branch structure and relatively short branch chains, amylopectin molecules undergo very limited intermolecular associations and retrograde very slowly (although they may gradually crystallize somewhat with time) [32]. Thus, waxy starches, which consist primarily of amylopectin, lack the ability to form strong gel networks. Starch paste characteristics are defined by: (1) the rheology of the continuous phase, (2) the rigidity of granule remnants and the volume occupied by them, and (3) the extent and nature of interactions between the continuous and dispersed phases [30].

Short and long flow are terms that remain in use within the starch industry to describe the nature of a starch paste, although they have been largely replaced by more exact rheological characteristics (Section 5.2.3). Short and long flow refer to the draining behavior from a pipette or funnel. As the forming drop gets larger, it becomes heavier and the flow rate increases. If the weight of the stream causes it to break so that the fluid exits in small drops, the fluid is said to have a short flow. Such a fluid is pseudoplastic, i.e., shear-thinning. Fluids without shear-thinning behavior exit in long strings (long flow, slimy texture).

### 5.2.1. Melting/Gelatinization

Melting and gelatinization transitions of starches are endothermic in nature and may be both detected and quantified via differential scanning calorimetry (DSC). Due to the heterogeneous nature of crystallites present within granules, starch thermal transitions occur over a temperature range rather than at a defined temperature.

At low moisture levels (water/starch ratios < 1:1), the term “melting” is used to define the disappearance of starch crystallinity in response to heating [31]. Melting of native starch produces up to four endothermic transitions – the first two being associated with disordering of amylopectin double helices and the latter two reflecting order to disorder transitions of complexes of amylose with the native lipids of the starch granules [30]. Thermal transitions occurring under limited moisture conditions (as low as 11%) are generally shifted to elevated temperatures (as high as 180 °C), depending on the amount of water present for plasticization [30, 31]. Melting phenomena are likely to be encountered within high-temperature/low-moisture processes such as extrusion or baking of low-moisture products.

Gelatinization, which is characterized by the thermal disordering of starch (amylopectin) crystallites in excess water (water/starch ratios > 1.5:1) [31], generally occurs over a 10–15 °C temperature range [30]. Thus, a gelatinization endotherm obtained via DSC is defined by an onset ( $T_o$ ), peak ( $T_p$ ), and completion ( $T_c$ ) temperature, as well as a gelatinization enthalpy ( $\Delta H$ ). For a native normal starch (i.e., amylose content in the range of 20–30%), the gelatinization temperature range generally falls between 55 and 80 °C, with the precise temperature range being specific to the botanical source of the starch [16, 30, 33]. High-amylose starches exhibit much higher and broader gelatinization temperature ranges (70–130 °C) relative to normal starches due to their abundance of long amylopectin branch chains [16, 33]. Aside from the events described for gelatinization, a second endothermic event (90–120 °C) may be observed for starches possessing amylose–lipid complexes (V-structures) (Chap. 4) [30, 31].

Starch gelatinization temperatures and ranges are impacted by the presence of other system constituents, particularly solutes. Sugars generally tend to increase the starch gelatinization

temperature, but reduce the gelatinization temperature range [30]. Hypotheses proposed to explain this effect include competition of sugars with starch for water (solvent), physical sugar–starch interactions, and/or anti-plasticization effects of the sugar–water cosolvent [30, 31]. Low salt concentrations inherent to most foods may increase the starch gelatinization temperature; salt effects on gelatinization become much more varied and complex at high (salt) concentrations [30]. Monoacyl and other polar lipids, either native or incorporated, may increase starch gelatinization temperatures due to complexation with amylose chains [31]. At typical concentrations encountered in food systems, hydrocolloids exhibit minimal impact on starch gelatinization characteristics (as measured by DSC) [30], although they do significantly influence starch paste rheology (Section 5.2.3).

### 5.2.2. Retrogradation

Retrogradation involves reassociation (crystallization) of starch chains within a paste upon cooling (below  $T_m$ ) to form either a viscoelastic gel network or a precipitate [31]. Although amylose and amylopectin chains are both capable of crystallization, the two polymers retrograde on vastly different timescales, with amylose crystallization being very rapid (minutes to hours) and amylopectin reassociation being very slow (days to weeks). For starch pastes comprised of both amylose and amylopectin, gelation involves both phase separation (formation of polymer-rich and polymer-deficient regions) and crystallization (primarily involving amylose chains), although the precise sequence of these two events is not fully resolved [30, 31]. Junction zones within normal starch gels are comprised almost exclusively of aggregates of amylose double-helical chain segments [30].

Starch crystallization is defined by three primary processes: nucleation (crystal initiation), propagation (crystal growth), and maturation (crystal perfection), of which nucleation is the rate-limiting step [30]. For starch pastes of less than 50% by weight concentration, nucleation is most favored at temperatures approaching  $T'_g$  (ca. –5 °C), whereas propagation (i.e., crystal growth) is enhanced at temperatures approaching the melting temperatures of the crystallites ( $T_m$ )

[30]. A hold or storage temperature of less than 60 °C, promotes formation of B crystallites (Section 5.1) [30]. The melting temperatures of amylose and amylopectin crystallites differ dramatically (140–160 °C and 45–60 °C, respectively), with amylose associations being much more thermoresistant [30]. Retrogradation may be monitored via a multitude of techniques including DSC, gel turbidity, light scattering, optical rotation, FTIR, NMR, and viscometry [30]. Within foods, excessive starch retrogradation often leads to product defects, such as syneresis, loss of viscosity, or staling of bakery products (amylopectin crystallization is thought to have a partial role here). Conversely, retrogradation may also be considered beneficial to various food products and processes (e.g., in the preparation of croutons, frozen potato products, and resistant starch) and may be promoted via defined cooling and/or temperature cycling schemes. Retrogradation is very much a phenomenon to be avoided in papermaking processes, particularly in sizing and coating operations.

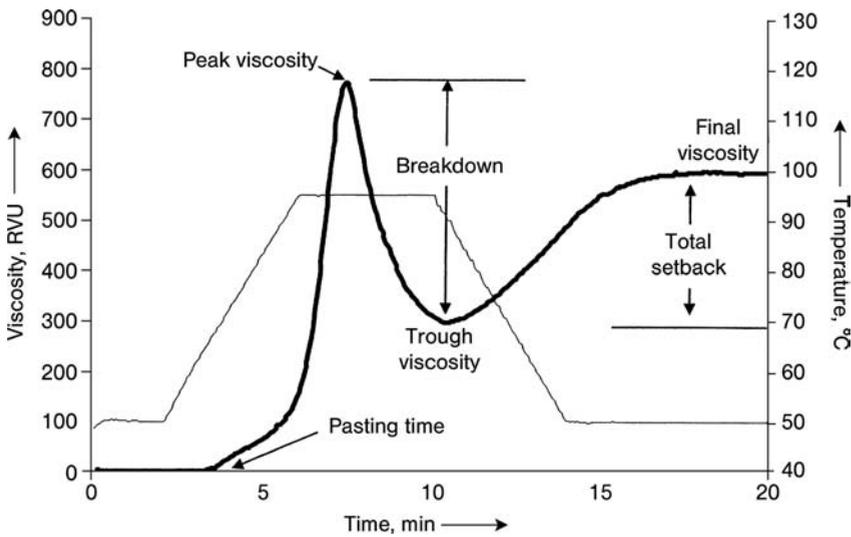
The tendency for a starch to retrograde can be decreased through chemical modification (i.e., stabilization; Section 9.1.3). Starch retrogradation may also be greatly influenced by other system components, though the specific roles of particular classes of constituents are often varied and difficult to categorize in unified fashion. However, there is reasonable consensus for the effects of monacyl and polar lipids, which generally decrease the extent of retrogradation by promoting formation of amylose-lipid complexes (Chap. 4) [30, 31], although the reverse has also been reported. Effects of various low-molecular mass sugars and oligosaccharides on starch crystallization vary according to the stereochemistry of the solute. Generally, solutes that exhibit favorable hydrogen bonding interactions with the native water structure are suggested to reduce starch crystallization, whereas solutes that disrupt the water network tend to promote starch retrogradation [30]. Water-soluble polysaccharides can enhance the starch retrogradation rate (via phase separation and concentration of starch polymer microdomains), but may either increase or decrease gel rigidity depending on the specific hydrocolloid added [30, 31]. In general, nonstarch polysaccharides tend to enhance the water-holding capacities and freeze-thaw behaviors of starch gels [31, 34].

### 5.2.3. Pasting and Viscoelastic Properties

Upon cooking in excess water, a starch granule slurry experiences dramatic physical changes in response to swelling, gelatinization, pasting, and retrogradation events. A pasting profile provides a definitive, systematic fingerprint that embodies the flow behavior of a starch-containing material as it undergoes these defined events. While the *Brabender ViscoAmylograph* was traditionally used for generating pasting profiles, the *Rapid Visco Analyser (RVA)* has now emerged as the instrument of choice, due to a smaller sample requirement for analysis, reduced analysis times, and a defined unit of viscosity measure (cP [mPa·s] or Rapid Visco Analyser Units [RVU]). (A *Brabender Micro Visco-Amylo-Graph* with similar functions as the RVA is also available [30].) A pasting profile is generated by these instruments by monitoring the viscosity of an aqueous starch suspension over the course of a specified heating-cooling cycle, in the presence of shear, over a defined analysis time period. Heating and cooling rates, length of hold, rate of shear, and heating and cooling temperatures may all be varied by the operator, though traditional profiles generally heat to 95 °C, hold at 95 °C, and cool to 50 °C. Defined pasting attributes (i.e., pasting temperature, peak viscosity, etc.) may be obtained at various points of a pasting profile to yield specific information about starch swelling properties, as well as paste stability and retrogradation tendency (Fig. 7).

*Pasting time* represents the point in time (for a defined heating rate) at which sufficient starch granule swelling has occurred to register an initial rise in viscosity (above that of the original ungelatinized granule slurry). This value is often reported in regard to temperature (i.e., *pasting temperature*). However, temperature values provided by the RVA instrument reflect the instrument heating block temperature rather than that of the actual paste. Thus, there is a lag in the true paste temperature relative to that of the heating block, although the extent of lag can be mathematically corrected to estimate the true paste temperature for a given heating rate value [35]. Pasting temperature provides an estimate of the minimum temperature needed to cook a starch under given slurry conditions [36].

*Peak viscosity* results from a rapid swelling of granules upon gelatinization. Paste composition



**Figure 7.** Example of a pasting profile depicting the viscosity of a wheat starch granule suspension over the course of a heating and cooling cycle. Specific pasting attributes obtained from the pasting profile are defined and labeled accordingly (bold line = starch viscosity profile; thin line = temperature profile)

at the peak is comprised of a combination of both highly swollen and ruptured granules within a continuous phase of solubilized starch. Peak viscosity is indicative of starch thickening power [30], and can be used to provide a rough estimate of the viscous load likely to be achieved in a cooking/mixing operation [36].

During the hold period at peak temperature (usually 95 °C), a starch paste will experience a loss in viscosity due to rupturing of the fragile, swollen granules until a *trough viscosity* (i.e., *hot paste viscosity*) is reached. (Trough viscosity represents the viscosity of the solubilized starch continuous phase containing dispersed granule remnants). *Breakdown* (peak viscosity minus trough viscosity) indicates the relative stability of a paste to high temperature and shear conditions. Chemical cross-linking of starch is conducted to stabilize granules against paste breakdown (Section 9.1.2).

Upon cooling a starch paste, amylose molecules begin to reassociate to form junction zones to achieve a *final viscosity*. *Setback* (final viscosity minus trough viscosity) reflects the extent of amylose recrystallization occurring within a starch paste, and is generally correlated positively with syneresis tendency [36]. Waxy starch pastes exhibit minimal setback, due to the lack of amylose. Normal starches, which generally exhibit a high propensity toward syneresis, may

be chemically substituted to reduce the tendency of the starch to retrograde (Section 9.1.3).

Beyond pasting properties, more sophisticated analysis of starch dispersion and/or gel properties may be conducted under conditions of constant stress or constant strain using uniaxial compression testing (both large and small deformation tests), a rotary viscometer, or a dynamic oscillatory rheometer [30]. These analyses determine starch viscoelastic properties, defined as the degree of solid-like (storage modulus,  $G'$ ) versus liquid-like (loss modulus,  $G''$ ) behavior present within a gel.

Nonstarch constituents present in a starch dispersion may have a significant effect on paste rheological behavior. High solute concentrations generally inhibit starch swelling, increase starch pasting temperature, and decrease paste peak viscosity [30]. Sugars may either increase or decrease gel strength, depending on their specific stereochemistry [30]; this effect was previously described in regard to retrogradation behavior (Section 5.2.2). Because of the essentially neutral character of starch, low concentrations of salts have little effect on gelation. Acids tend to decrease starch viscosity by promoting the hydrolysis of glycosidic linkages, effectively decreasing the molecular size of the starch polymers (Section 9.1.1). Polar lipids, through complexation with amylose chains (Chap. 4), restrict granule swelling, increase starch pasting

temperature, and reduce overall paste viscosity [31]. Hydrocolloid addition may alter starch pasting properties (pasting temperature, peak viscosity, breakdown, setback, final viscosity), as well as both the storage and loss moduli of starch gels, although both the nature and degree of effects vary according to the specific polysaccharide [34]. To explain these effects, direct starch-hydrocolloid interactions and/or phase separation of the mixed polymer gel system have been proposed [31, 34].

## 6. Minor Components of Starch Granules

In addition to amylose and/or amylopectin molecules, starches contain other components, including lipid, protein, and ash. Only cereal starches contain significant amounts of lipids. Normal cereal starches contain ca. 0.6–1.2% total lipid by weight, consisting primarily of free fatty acids and lysophospholipids of differing ratios and compositions in different starches. Starches without amylose, such as waxy maize starch, contain only ca. 0.2% lipid. Noncereal starches, such as potato starch and tapioca starch, contain less than 0.1% lipid. Normal cereal starches contain ca. 0.35–0.40% protein by weight, while waxy maize starch contains ca. 0.25% protein and potato and tapioca starches contain ca. 0.1% protein. Potato starch contains monostarch phosphate ester groups (0.06%–0.1% P by weight). Starch ash contents usually range between 0.1 and 0.5% and are related to the lipid, protein, and phosphate ester contents.

## 7. Starch Biosynthesis and Genetics

The biosynthesis of amylose and amylopectin has been and continues to be an area of intense study [37] due to the complex natures of the molecules, especially the clustered branching pattern of amylopectin, and because of the desire to understand the impact of the biopolymer structures on the properties of a starch. The genetics of starch biosynthesis has also received intense study [38] because of the potential importance of altering such characteristics as the amylose/amylopectin ratio and the fine structure of amylopectin.

## 8. Industrial Starch Production Processes

### 8.1. Corn/Maize Wet Milling

Production of corn starch occurs primarily in the USA, China, EU, Japan, South Korea, Brazil, and Argentina. Corn wet milling consists of several steps: (1) cleaning the grain, (2) steeping of kernels, (3) milling of kernels and separation of fractions (i.e., starch and nonstarch components), and (4) drying of the isolated starch [39].

#### 8.1.1. Grain Cleaning

Grain is first cleaned by screening and by magnetic means to remove foreign material including metal.

#### 8.1.2. Kernel Steeping

Cleaned grain is steeped to soften the kernel and to facilitate its separation into the desired components. This process involves countercurrent steeping in water containing 0.10% sulfur dioxide at 48–52 °C for 30–40 h. Sulfur dioxide aids in the dissolution of the protein matrix to release the starch, combats growth of spoilage organisms, and maximizes the starch yield. The proper steeping temperature is critical for optimal growth of lactic acid bacteria, which lower the pH, restricting the growth of other organisms. The lactic acid bacteria also release proteolytic enzymes, which break down protein. Steepwater pH is typically buffered at ca. 4.0.

Steepwater may be further processed to remove phytic acid. In either form, it is then concentrated and sold as a nutrient solution for commercial fermentation to produce, for example, antibiotics, or more often dried by absorption onto corn fiber and sold as cattle feed.

#### 8.1.3. Kernel Milling and Fraction Separation

After steeping, the grain is milled to obtain separation of components. Steeped grain is first put through an attrition mill to release the oil-

containing germ, which is removed using hydroclones (liquid cyclones, hydrocyclones) and dried prior to extraction with hexane or pressed to remove the oil. Next, the residual grain is ground to release starch granules. The slurry is then screened to separate the corn hull or seed coat, which is recovered as a fibrous mass.

Starch is isolated from the remaining slurry using centrifuges or by passage through batteries of hydroclones that separate out not only the starch, but also the insoluble protein (called *corn gluten* in the industry). The process also washes the starch to lower the protein and ash contents. The protein (gluten) is less dense ( $1.1 \text{ g/cm}^3$ ) than starch ( $1.5 \text{ g/cm}^3$ ) and is easily separated by centrifugal forces. Starch thus produced contains 1–2% protein, which may be removed by a second washing with water to give a starch with a final protein content of  $< 0.38\%$ .

The final starch slurry is recovered by filtration or centrifugation, and the starch cake is dried in continuous driers (usually flash driers) (Section 8.1.4) and sold as unmodified (native) starch. Alternatively, the starch slurry can be pumped, cooked, and subjected to enzyme-catalyzed hydrolysis to produce syrups and other products (Section 9.1.1), pumped into tanks for chemical modification (Sections 9.1.2, 9.1.3, 9.1.4), or pumped onto hot rolls for production of pre-gelatinized starch (Section 9.2.1).

#### 8.1.4. Starch Drying

Starch is usually dried by flash drying. In this method, the starch slurry is centrifuged or filtered and the moist starch cake is introduced at the bottom of a stream of rapidly moving hot air (93–127 °C). Drying is rapid and the starch is collected using cyclones. Drying parameters can be used to control both bulk density and particle size.

### 8.2. Wheat Starch

Wheat starch (along with starches of barley, rye, and triticale) is comprised of at least two distinct granule populations, commonly designated the A- and B-types. The respective A- and B-type granule populations possess different sizes ( $> 10 \text{ m}$  vs.  $< 10 \text{ }\mu\text{m}$ ), shapes (lenticular vs. spherical/

polygonal), and starch characteristics and properties [40–42]. Of the two primary granule types, A-type granules are most industrially important, although small granule starches (high B-type granule contents) are also produced commercially [41].

In contrast to corn wet-milling, commercial processes for wheat starch isolation involve dry-milling of grain to flour (72% extraction or greater), which is the preferred starting material for starch isolation. Most commercial wheat starch isolation methods take advantage of the matrix forming properties of gluten proteins, combined with the insoluble nature of starch granules, to facilitate simultaneous separation of starch and gluten coproducts. Wheat starch is isolated on a commercial scale by one of several methods, including the Martin (dough ball), batter, Fesca, Raisio, hydrocyclone (dough-batter), or high pressure disintegration/tricanter processes [41]. The latter two processes are most commonly employed industrially, with advantages of reduced energy and water usage. In short, the process utilizing hydrocyclones (hydroclones) involves kneading and vigorous agitation of wheat flour-water mixtures to agglomerate gluten into thread-like pieces, after which hydrocyclones are used to separate starch and gluten streams. A series of hydrocyclones is further utilized to concentrate and purify the primary starch stream (yielding a wheat starch with a high concentration of A-type granules). Gluten, small-granule starch (predominantly B-type granules), and fiber (pentosans) may be recovered via additional processing. The high-pressure disintegration/tricanter process utilizes a combination of high-shear homogenization and decanter centrifugation processes to efficiently fractionate wheat flour batters into A-type granule starch, B-type granule starch, gluten, and fiber product streams. The primary producers of wheat starch are France, Germany, USA, and China.

### 8.3. Potato Starch

Potato starch is produced in largest quantities in Europe, especially in the Netherlands, Germany, and France [43]. Potato starch is also produced in China in substantial amounts. Industrial potatoes are washed with water to remove dirt and other foreign matter. They are then disintegrated in the

presence of an antioxidant using drum rasps. Potato juice is removed using a decanter centrifuge. Sieving is used to remove fiber. After sieving, a disk-type, continuous centrifuge is used to concentrate the starch granules and remove any remaining small particles of fiber and protein. Although starch granules within potatoes occur in a wide range of sizes (see Table 3), the larger granules are primarily obtained in this process. Any remaining protein is removed by reslurrying the starch in water and concentrating the starch using a series of hydroclones in a countercurrent fashion. The starch is then collected by filtration and dried to ca. 20% moisture.

In the USA, potato starch is recovered commercially as a coproduct of potato processing operations, viz. slicing. Recovered starch is further washed and dried.

#### 8.4. Tapioca/Cassava Starch

Tapioca starch is obtained from roots of the cassava plant, which is grown in tropical areas and is variously known as cassava, cassada, yuca, manioca, mandioca, and tapioca, depending on the region where it is grown [44]. Roots are harvested 10–12 months after planting and processed as quickly as possible. Processing consists of washing the roots, then converting them into a pulpy slurry that is passed through a series of screens to remove fiber. The resulting slurry of starch granules is concentrated and dewatered via centrifugation. Finally, the starch is dried. The yield of starch is ca. 26% (based on the fresh weight of roots of 60–70% moisture content).

#### 8.5. Rice Starch

Most rice starch is prepared by steeping broken milled rice kernels in 0.3–0.5% NaOH solution at 25 °C to 50 °C for times of up to 24 h [45]. Steeping in an alkaline solution softens the kernels and dissolves the glutelin protein, which constitutes approx. 80% of the total protein in rice. Wet-milling of the steeped kernel produces a slurry of starch. An additional holding of the alkaline slurry for 10–24 h further solubilizes the proteins. Fiber is removed using screens or filters, and the starch is isolated from the slurry, washed, neutralized, and dried. Rice starch may also be

produced by a mechanical process which involves physical separation of starch granules and protein bodies.

### 9. Modified Starches

The terminology related to modified starches, as with other terminology used in the starch industry, is not always precise. In this article, starches that are modified by reaction of their hydroxyl groups with a chemical reagent to convert them into esters, ethers, or other chemical derivatives, such as graft copolymers, are called *derivatized starches*. Those that are modified by some change in the basic polymer structure or molecular mass (by acid or enzyme treatment or oxidation) are called *converted* or *thinned starches* (Section 9.1.1). Starches that have undergone a physical (thermal) treatment are described by the nature of the product, most often being a type of *pregelatinized starch* (Section 9.2). Any starch treated in any way to alter one or more of its original physical or chemical properties is called a *modified starch*. A modified starch may be multiply-modified, e.g., derivatized, converted/thinned, and/or pregelatinized.

Native starches have low process tolerance and, in the case of food starches, generally produce undesirable textures. Their pastes often have poor stability. Conversion and/or derivatization produces higher quality products. Companies that produce and market starches make available a number of products that are the result of various combinations of starch type and modification. Converted, derivatized, and unmodified starches from different sources are often employed in the same general applications by different users.

Uses of native starches are limited because, as indicated above, their inherent physiochemical properties make them less than optimally desirable for most applications. Rather, the majority of starches used in various food and other industrial applications are modified starches. There are several reasons for modifying the properties of starches, but the two principal ones may be the following: (1) to prevent the formation of precipitates or microgel particles in a starch paste or gelation of the entire paste (Section 5.2.2), and (2) to reduce the viscosity of a starch paste (Section 5.2.3) so that higher solids solutions

can be made. Both are needed for starch products used in the papermaking process. For starches used in processed food products, additional factors are important. In foods, starch ingredients provide bulk, body, and improved texture and mouthfeel, as well as other functionalities. For most applications, food processors prefer starches with better behavioral characteristics than those provided by native starches. Upon being cooked into slurries, native (i.e., unmodified), corn (maize) and waxy corn (waxy maize) starches produce weak-bodied, cohesive, rubbery pastes and undesirable gels. However, their functional properties can be improved dramatically by modification. In general, modifications are made to increase the ability of the paste produced by cooking to withstand the heat, shear, and low pH associated with processing conditions, to make the starch paste more stable, or to introduce specific functionalities.

Modifications can be accomplished by chemical (the majority) or physical treatments. Types of modifications include cross-linking of polymer chains (Section 9.1.2), non-cross-linking derivatization (sometimes called *stabilization* [Section 9.1.3] and depolymerization (Section 9.1.1) (all chemical modifications) and pregelatinization (a physical modification) (Section 9.2). Many improvements in the properties of a starch can be made with these modifications, singly or as combinations of them. Some specific property improvements that can be obtained are reduction in the energy required for cooking, modification of cooking characteristics, increased solubility, increased or decreased paste viscosity, increased freeze-thaw stability of pastes, enhancement of paste clarity, increased paste sheen, enhancement or reduction of gel formation and/or gel strength, reduction of gel syneresis, improvement of interaction with other substances, improvement of stabilizing properties, enhancement of film formation, improvement in water resistance of films, reduction in paste cohesiveness, and increased stability of the granules and pastes to lower pH, heat, and shear. Such imparted characteristics are itemized in Table 4.

The most important commercial derivatives of starch are those in which only a very few of the hydroxyl groups are derivatized. Normally, the hydroxyl groups of the starch polymer molecules are converted into ester or ether groups at very

**Table 4.** Characteristics imparted by primary starch modifications

Modification	Main Attributes
Hypochlorite-oxidized	Whiter Lowered gelatinization temperature Reduced maximum paste viscosity (usually) Softer, cleaner gels Greater adhesion of pastes
Cross-linked (food)	Increased stability to heat Increased cooking temperature (delayed pasting) Increased shear resistance Increased stability to low pH/acid Decreased setback of cooks Decreased or increased paste viscosity Increased body
Stabilized	Lowered gelatinization/pasting temperature (easier cooking) Improved tolerance of cold storage of products Improved freeze-thaw stability of products Decreased paste setback/retrogradation Reduced gelation More easily dispersed when pregelatinized Greater paste clarity Increased moisture control
Cross-linked and stabilized	Lowered gelatinization/pasting temperature, but increased paste viscosity Other attributes of cross-linking and stabilization A variety of textures and rheological properties
Octenylsuccinylated	Emulsifying properties Emulsion-stabilizing properties Ability to encapsulate hydrophobic materials
Thinned	Reduced hot-paste viscosity Lowered gelatinization/pasting temperature Increased solubility Increased gel strength Increased paste clarity or opacity Increased film-forming capability
Dextrinized	Imparts crispness (food) Increased stability (food) Reduced viscosity Improved film formation Emulsifying properties Increased browning (food) Increased adhesion of pastes Remoistenable adhesiveness
Pregelatinized <sup>a</sup>	Thickening without cooking

<sup>a</sup>Including cold-water swelling.

low *degree of substitution* (DS) values, the DS being the average number of hydroxyl groups per glucosyl unit that have been derivatized by ether or ester formation. DS values of modified food starches are most often < 0.1 and are generally in

the range 0.002–0.2. Thus, generally, on average, there is one substituent group for every 5 to 500 D-glucopyranosyl units.

Starches are chemically modified as an aqueous slurry of granules. For esterification or etherification, a starch slurry of 30–40% solids is introduced into a stirred reaction tank. Sodium sulfate or sodium chloride is added to a 10–30% concentration to inhibit gelatinization. The pH is adjusted, generally with sodium hydroxide, to pH 8–12, the exact value depending on the reaction to be conducted, after which the chemical reagent is added to the starch slurry. The alkaline pH activates the starch for reaction by converting some of its hydroxyl groups to alkoxide ions for participation in nucleophilic substitution reactions. The reaction temperature is generally maintained at less than 60 °C, often to 49 °C, to prevent pasting of the granules so that the derivatized starch can be recovered in granule form. Following reaction to the desired degree of substitution, the starch is recovered by centrifugation and/or filtration, washed, and dried.

## 9.1. Chemically Modified Starches

### 9.1.1. Converted Starches and Hydrolyzates

In the starch industry, the term *conversion* refers to depolymerization. Products that are partially depolymerized are called *converted starches*. There are three basic processes for making converted starches: using an acid (with various moisture contents and degrees of heating), using an enzyme(s) [amylase(s)], using an oxidant in an alkaline system. Extensive conversion produces *maltodextrins*, *syrup solids*, *syrups*, and *dextrose*.

#### 9.1.1.1. Thinned Products

To produce products variously known as *acid-modified*, *acid-converted*, *converted*, *thin-boiling*, *fluid*, or *fluidity* starches [46–48], which are the least converted of the products converted with an acid, either hydrochloric acid is sprayed onto well-mixed starch or stirred moist starch is treated with hydrogen chloride gas, and the mixture is heated until the desired degree of

hydrolysis (which is very slight in any case) is obtained. The acid is then neutralized, and the product is recovered by filtration or centrifugation.

When to stop a conversion is usually determined empirically by monitoring the viscosity of a hot paste of the acid-modified starch. In the starch industry, this is known as determining *fluidity*. Acid conversion is practiced on both native starches and chemically modified starches, i.e., derivatized starch products (Sections 9.1.2, 9.1.3) may also be *thinned*, in which case, the pH of a stirred slurry of starch granules (36–40% solids) that has just been derivatized and held at a temperature below the gelatinization temperature of the derivatized starch (usually 40–60 °C) is lowered by the addition of a mineral acid, such as hydrochloric acid, until it is in the acid range. When the desired degree of limited hydrolysis (conversion) is reached, the suspension is neutralized and the granules are recovered by centrifugation and/or filtration, washed, and dried.

Compared to the parent starch, acid-converted starches undergo a greater degree of granule disintegration upon cooking and produce pastes with lower intrinsic viscosity values, reduced hot paste viscosity, increased gel strength, and better film-forming capabilities (Table 4). Specific characteristics are a function of the parent starch and the conversion conditions.

Many starch products are bleached with small amounts of an oxidant. Use of higher levels of an oxidant oxidizes the starch and often results in partial depolymerization. Conversion using an oxidant and an alkaline system occurs because oxidation of a hydroxyl group of a D-glucopyranosyl unit introduces a carbonyl group and leads to  $\beta$ -elimination and chain cleavage. Such a reaction is usually accomplished by treating a slurry of starch granules with a solution of sodium hypochlorite [49]. Use of hydrogen peroxide and cupric ions depolymerizes starch molecules without introducing carbonyl groups. Ammonium persulfate is used to depolymerize starches oxidatively for paper sizing and coating processes. The decision as to when to stop an oxidation is generally determined in the way previously noted for an acid-converted starch, i.e., by monitoring hot paste viscosity (fluidity).

Properties of starches converted by oxidative cleavage generally parallel those of starches

converted by acid-catalyzed hydrolysis, but with two differences. Pastes of oxidized starches generally are clearer and more stable than those made from acid-modified starches, and there can be greater variability in products in oxidatively-thinned products due to choice of the parent starch, oxidizing agent, and conditions of oxidation. For example, starches treated with low levels of hypochlorite at an acidic pH (rather than the usual alkaline pH condition) result in products with a greater (rather than reduced) hot paste viscosity.

Thinning is primarily done so that higher solids solutions can be made without generating excessive viscosity.

### 9.1.1.2. Starch Dextrins

Starch dextrins [9004-53-9] are products resulting from a greater degree of conversion than are thinned products. *Dextrinization* is the process of making dextrins.

Starch dextrins (occasionally called pyrodextrins) are made by heating a starch with or without addition of an acid [46–50]. There are three general types of these dextrins: white dextrins, yellow dextrins, and British gums. The variables involved in making dextrins are the base starch used, the amount and type of acid used, the percentage of moisture in the starch, the temperature employed, and the time of conversion. In general, white dextrins are made using an acid catalyst, relatively low temperatures, and short conversion times. Yellow dextrins are products of higher temperatures and longer conversion times. British gums are also made using high temperatures and long times, but with less or no added acid. Hydrochloric acid is usually the acid used, particularly for food-grade dextrins. Starch at 10–22% moisture is either treated with gaseous hydrogen chloride or a solution of hydrochloric, sulfuric, or phosphoric acid is sprayed onto the starch as an atomized mist. The starch is then predried to a moisture content of 2–5% by heating it at a relatively low temperature, sometimes under reduced pressure, to keep hydrolysis to a minimum. During the actual dextrinization step (pyroconversion), the pre-dried starch is heated at 100–200 °C. The product is then cooled and rehumidified. Alternatively, the starch is first dried to a moisture content of 2–5% and is then

treated with HCl (either as a gas or sprayed on in liquid form) before being heated.

Three types of reaction take place during dextrinization, the relative amounts of which are a function of the moisture content of the starch and the treatment temperature. (1) Hydrolysis of glycosidic bonds is the predominant reaction when the moisture content is high and is, therefore, the main reaction in the preparation of white dextrins with a low degree of conversion. Because of glycosidic bond cleavage and the resulting reduction in polymer molecular masses, final products generate lower solution viscosities. (2) Transglycosidation (transglycosylation) results in transfers of portions of glucan chains to hydroxyl groups on the same or different chains to create new glycosidic bonds. The result is more highly branched and more soluble macromolecules. (3) Repolymerization (reversion) occurs with catalytic amounts of acid at high temperatures and low moisture contents. Under these conditions, glycosidic bonds are formed from the reducing ends of the maltooligosaccharides (and any glucose) released during hydrolysis. The result is higher molecular mass and more highly branched macromolecules than were present before reversion occurred.

### 9.1.1.3. Dextrose Equivalency

Converted, i.e., depolymerized, products are classified by their *dextrose equivalency (DE)* which is defined as  $100 \times DP$  (*degree of polymerization* or the average number of D-glucosyl units in the polymer or oligomer). The DE value is based on the facts that (1) a new reducing end-unit is generated with each hydrolytic cleavage of a starch polymer chain and (2) the reducing power of converted products is something that can be measured. Amylose and amylopectin have no measurable reducing power (DE = 0). The product of complete hydrolysis, D-glucose (dextrose) [50-99-7] (DP = 1), has by definition a DE of 100. Therefore, the DE of a product of starch hydrolysis is its reducing power as a percentage of the reducing power of dextrose and is inversely proportional to the average molecular mass of the product molecules. (Both DE and DP are average values for populations of molecules.)

#### 9.1.1.4. Maltodextrins

Maltodextrins [9050-36-6] by regulatory definition (USA) are purified, nutritive mixtures of saccharide polymers obtained by partial hydrolysis of edible starch [51–53]. Most molecules in maltodextrin preparations are maltooligosaccharides of DP 2–20. Because the DE values of the products are mostly in the range 5–15, their average DPs are in the 7–20 range. Maltodextrins are produced by hydrolysis of the starch molecules within pastes using either a single amylase, several amylolytic enzymes, or an acid to achieve DE values of less than 20 (average DP >5). Maltodextrins made by acid-catalyzed hydrolysis alone possess a high quantity of linear chains that are able to retrograde. When it follows acid-catalyzed hydrolysis to DE 5–10,  $\alpha$ -amylase-catalyzed hydrolysis produces maltodextrins of low hygroscopicity and high water solubility that generate less haze when dissolved. Maltodextrins are also produced either by use of an  $\alpha$ -amylase alone or with a combination of an  $\alpha$ -amylase and a debranching enzyme.

Maltodextrins that have been specially prepared so that they associate to form microcrystals that are about the size of oil or fat droplets may be used as fat mimetics/sparers/replacers. Another specially made maltodextrin, one in which digestible carbohydrate has been removed, is employed as soluble dietary fiber.

Maltodextrins are primarily used in processed food products; their collective attributes are listed below.

- Bland flavor
- Control moisture migration
- Crystallization inhibition
- Encapsulator of flavors and aromas
- Fat replacers, spacers, and mimetics (specially prepared maltodextrins in microcrystalline form)
- Film formers
- Good dispersibility in aqueous systems
- Good solubility in aqueous systems
- Low to no sweetness
- Provide body
- Provide a smooth texture
- Range of susceptibility to Maillard browning
- Readily digestible
- Spray dry easily

#### 9.1.1.5. Syrup Solids

Hydrolysis to DE 20–35 (average DP 3–5), followed by drying, produces syrup solids.

#### 9.1.1.6. Syrups and Crystalline D-Glucose (→ Glucose and Glucose-Containing Syrups)

Continued hydrolysis of starch with an acid and/or enzymes produces mixtures of D-glucose, maltose, and other maltooligosaccharides in a concentrated form known as *glucose syrups* (usually called *corn syrups* in the USA) [54–57]. Most often, a glucose syrup is a purified, concentrated, aqueous solution of nutritive saccharides derived from food-grade starch with DE values of > 20. (Syrups that are not required to be food grade are also produced for use in anti-freeze and deicing compositions.)

Glucose syrups are made by one of three processes: (1) acid conversion (pH ca. 2, temperature > 100 °C) (a minor process); (2) acid-enzyme conversion (an acid-converted hydrolyzate is treated with one or more hydrolyzing enzymes, the choice of which depends on the desired saccharide profile of the finished syrup); or (3) enzyme-enzyme conversion (the major process) (in a single step, a starch suspension is pasted and the paste is liquefied using a thermostable  $\alpha$ -amylase. The product is then treated with one or more other enzymes depending upon the desired saccharide profile). Specifically, glucose syrups are most often made by passing an aqueous slurry of starch containing a thermally stable  $\alpha$ -amylase through a jet cooker, where rapid gelatinization and enzyme-catalyzed hydrolysis (*liquefaction*) occur. After the solution is cooled to 55–60 °C, glucoamylase is added and hydrolysis is continued. When hydrolysis is complete, the syrup is clarified, decolorized, and concentrated. DE values of syrups may range from 25 to 95 with the lower-DE syrups having greater proportions of maltooligosaccharides and the higher-DE syrups having a greater proportion of D-glucose. Syrups are stable because the oligosaccharides present in them prevent crystallization and the high osmolality (ca. 70% solids) prevents growth of microorganisms. When crystalline D-glucose (dextrose) [50-99-7] or its monohydrate is desired, seed crystals are added to a syrup of DE > 95

[54, 56]. *High-maltose syrups* are also produced, as well as being used as is; they are the starting materials for the production of maltitol [585-88-6] [57].

#### 9.1.1.7. High-Fructose Syrups and Crystalline D-Fructose

For the production of D-fructose [57-48-7], a solution of D-glucose is passed through a column containing immobilized glucose isomerase, producing an equilibrium mixture of approximately 58% D-glucose and 42% D-fructose [56-58]. Higher concentrations of D-fructose are desired for many applications of *high-fructose syrups* (HFS), often called *high-fructose corn syrups* (HFCS) in the USA. To make HFS/HFCS with more than 42% D-fructose, the isomerized syrup is subjected to a continuous chromatographic separation process by passing it through a bed of cation-exchange resin in the calcium salt form that binds D-fructose; the resin is subsequently eluted to provide a fraction enriched in D-fructose. This fraction is added to a 42% fructose solution to produce syrups with higher concentrations of D-fructose. Two major types of high-fructose syrups are produced: HFS 42 (ca. 42% fructose) and HFS 55 (ca. 55% fructose). Although D-fructose is not easily crystallized, crystalline D-fructose can be obtained from the enriched solution [59].

#### 9.1.1.8. Other Starch Conversion Products

Other commercial products of starch conversion include  $\beta$ -cyclodextrin [7585-39-9] [60] and  $\alpha,\alpha$ -trehalose [99-20-7] [57].

#### 9.1.2. Cross-linked Starches

Cross-linking reactions utilize bi- or multifunctional reagents to induce formation of intramolecular and/or intermolecular cross-links between adjacent starch chains within starch granules. Reagents employed for the commercial production of cross-linked starches include phosphoryl chloride (phosphorus oxychloride,  $\text{POCl}_3$ ), sodium trimetaphosphate (STMP), epichlorohydrin (EPI), and adipic-acetic mixed anhydride [61, 62]. Reaction conditions

and schemes vary according to reagent type. For reaction with STMP, starch granules are impregnated with solutions containing both reagent and a catalyzing base, after which slurry moisture levels are reduced to less than 15% and granules are heated to 130 °C in the semi-dry state to drive the reaction [63]. For cross-linking with STMP, reaction is favored at pH values above 10. In contrast,  $\text{POCl}_3$ , EPI, and adipic-acetic mixed anhydride reagents are reacted with starch granules in aqueous slurries at pH values of 11-12, 8, and 10.5, respectively [62]. Products of cross-linking reactions are in the form Starch-O-X-O-Starch, where X represents  $-\text{PO}_2^-$  for reactions with  $\text{POCl}_3$  and STMP,  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$  for reactions with EPI, and  $-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}-$  for reactions with adipic-acetic mixed anhydride.

Starch cross-linking reactions are employed to strengthen the structure of swollen granules upon gelatinization (Section 5.2.1), imparting resistance to viscosity breakdown (Section 5.2.3) in the presence of mechanical shear, acid conditions, and/or high temperatures. Cross-linked starch rheology is ultimately defined by the nature and concentration of swollen granules within a paste, with the firmness of swollen granules increasing with increasing cross-linking levels (Section 5.2.3). Cross-linked starches typically possess one cross-link for every 100-3000 glucosyl units. Properties of the products vary with modification level. Very low levels of cross-linking usually stabilize the granule structure, allowing the modified starch to attain a higher degree of granule swelling during heating than would be observed for the unmodified native starch. In such cases, higher swelling powers and paste peak viscosities are generally observed (Section 5.2.3). Progressively higher levels of cross-linking generally lead to reduced granule swelling, solubility, extent of amylose leaching, paste clarity, and paste peak viscosity (see Table 4). Those products with significantly reduced peak viscosities are known as *inhibited starches*. Cross-linked starches generally possess improved paste texture (i.e., are less stringy), but do not generally exhibit stability to retrogradation or freeze-thawing without additional stabilization (i.e., dual modification) (Section 9.1.3).

### 9.1.3. Stabilized Starches

*Stabilization* (also called *substitution*) involves derivatization of a starch with a monofunctional reagent [64], converting starch hydroxyl groups to ester or ether groups depending on the reagent used. Both starch esters and ethers are produced under similar reaction conditions. Derivatization is most often conducted in the form of an aqueous granule slurry (30–40% solids) in the presence of a gelatinization-inhibiting salt (10–30% concentration; most often sodium sulfate, sometimes sodium chloride) between pH values of 8 and 12, the optimum pH being reagent specific. The temperature of the reaction medium is typically adjusted (most often to 49 °C) to further promote starch granule swelling and reactivity. Use of a gelatinization-inhibiting salt and a temperature below the gelatinization temperature of both the native starch and the modified product prevents pasting, allowing the starch to be recovered in granular form. Allowed DS/MS levels of products intended for use in foods vary from country to country (with those within the EU being uniform), but generally range from 0.002 to 0.2, with different maximum values for different reagents (as examples, maximum allowable derivatization levels for food ingredient products are noted in the ensuing discussion where appropriate).

Commercial monostarch esters include starch acetates (Starch-OCOCH<sub>3</sub>), succinates (Starch- O-CO(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub><sup>-</sup>), octenylsuccinates (Starch-OCOCH[CH<sub>2</sub>CO<sub>2</sub><sup>-</sup>]CH=CH(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), and phosphates (Starch-OPO<sub>3</sub><sup>2-</sup>). Acetylated starch (maximum allowable DS ~ 0.09) is prepared using acetic anhydride or, in countries in which possession of acetic anhydride is prohibited, vinyl acetate [65]. Starch succinates are made by reaction with succinic anhydride, but are of limited commercial significance [66]. Reaction of starch with oct-1-enylsuccinic anhydride (OSA) produces the oct-1-enylsuccinic ester (OSA starch), for which the DS may not exceed 0.02 [66]. Monostarch phosphate esters are generated from reaction of starch with sodium orthophosphate or sodium tripolyphosphate (STTP) [67]. A DS maximum of 0.002 is permitted for monostarch phosphate esters. A large variety of other esters can be, and have been, made by selection of the proper reagent [65, 68]. These other esters include starch and amylose

triacetate, which are water insoluble, thermoplastic materials (Section 9.2.4).

Manufactured monostarch ethers include hydroxyethyl (Starch-OCH<sub>2</sub>CH<sub>2</sub>OH), hydroxypropyl (Starch-O-CH<sub>2</sub>CHOHCH<sub>3</sub>), carboxymethyl (Starch-OCH<sub>2</sub>CO<sub>2</sub><sup>-</sup>) and cationic (discussed in Section 9.1.4) starches. Reaction with ethylene oxide produces hydroxyethyl starch [68, 69], reaction with propylene oxide produces hydroxypropyl derivatives (maximum MS 0.2) [68, 70], and reaction with sodium monochloroacetate produces sodium carboxymethyl starch [71], known as sodium starch glycolate in the pharmaceutical industry. A large variety of other ethers, including silyl ethers, can be made by selection of the appropriate reagent [68].

Esterified and etherified products generally exhibit similar physical properties, although ethers are stable to acids and bases, while esters are not. In general, *stabilized starches* are so named because they have a reduced tendency to undergo retrogradation (usually a very desirable attribute) due to the incorporation of bulky substituent groups along the starch chains, that block intermolecular associations. Some incorporated substituent groups also possess a negative charge (e.g., monostarch phosphate esters), further reducing interchain associations (through like-charge repulsion) to enhance paste stability. Thus, stabilized starches produce more stable starch pastes and gels with improved clarity, less syneresis, and greater freeze-thaw stability than their unmodified starch counterparts (see Table 4). Substitution (especially at high levels) can disrupt the native granule structure, resulting in reduced starch gelatinization and pasting temperatures, as well as increased starch swelling, paste peak viscosities, and solubilities. In the case of OSA starch, some hydrophobicity is also introduced to starch chains, giving the product emulsifying and emulsion-stabilizing properties (Table 4). Stabilization-type reactions are often conducted in combination with other types of chemical and/or physical modifications to yield multifunctional starches (Section 9.4).

### 9.1.4. Cationic Starch

Cationization reactions are carried out using monofunctional reagents that impart a positive charge to starch chains via derivatization with

reagents that incorporate ether groups containing imino, amino, ammonium (quaternary amino), sulfonium, or phosphonium moieties [72]. The most industrially significant and commonly utilized reagent for starch cationization is 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTMA) [72–74], although a multitude of potential reagents may be employed. Reaction with CHPTMA gives the following product: Starch-O-CH<sub>2</sub>CHOHCH<sub>2</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>.

Cationic starch may be prepared batchwise via granular slurry, semi-dry, and solubilized paste processes, and by continuous means such as reactive extrusion [73–75]. The first two processes yield a modified starch product with retained granule structure, while in the latter two processes starch is reacted in a gelatinized or molten state [75]. For the granular slurry process, reaction may be conducted in either an aqueous or aqueous alcohol reaction medium in the presence of NaOH at a temperature of 49 °C to achieve reaction efficiencies in the range of 80–88% [72–75]. Aqueous slurry reactions generally include sodium sulfate to prevent gelatinization of the starch granules during reaction, while use of an aqueous alcohol reaction medium eliminates the need for a gelatinization-inhibiting salt [75]. The semi-dry cationization process, which also maintains starch in a granular form, entails heating of dry granular starch (< 120 °C) in the presence of both catalyst (NaOH) and reagent [75], resulting in reaction efficiencies of 90–95% [74]. For cationization via the paste process, a starch slurry is adjusted to alkaline pH (ca. 11.3) and gelatinized via steam injection, prior to reaction at 50 °C [76]. The use of an extruder as a continuous reaction vessel (i.e., reactive extrusion) for derivatization of starch polymers in the molten state has been described for various types of modification [75]. For starch cationization, the reactive extrusion process is reported to achieve reaction efficiencies in the range of 90% [77–79]. However, the high temperature and shear conditions imposed by the extrusion process result in some thermomechanical degradation of starch molecules, the degree of which is dependent on the processing parameters [80, 81].

For cationic starches modified in granular form, relative starch crystallinities, gelatinization temperatures and enthalpies, and pasting temperatures decrease with increasing levels of

cationization [72, 73]. Cationic starch derivatives also exhibit increased swelling powers, water sorption properties, peak and breakdown viscosities, stability of pastes and gels to syneresis, lipid-binding capacity, and emulsion-stabilizing properties relative to native (unmodified) starches [72, 73].

The primary applications of cationic starches are in the wet-end, surface-sizing, and coating processes in the paper industry, as well as industrial flocculants in sludge dewatering and mineral ore recovery operations [72–74]. Degree of substitution (DS) values for cationic starch derivatives used in papermaking applications generally range from 0.02–0.07, while those for flocculent applications are significantly higher (DS ca. 0.2–0.7) [73].

### 9.1.5. Starch Graft Copolymers

Starch graft copolymers are derivatives in which synthetic polymers are covalently bonded to starch molecules, most often through ether linkages. These products are generally obtained by generating free radicals from hydroxyl groups of native or hydroxyalkylated (generally hydroxyethylated) starch molecules, followed by reaction with an unsaturated monomer, such as an acrylic or vinyl monomer. A wide range of different products has been made using different methods for producing starch free radicals, different polymerizable monomers, and different starches and modified starches [82, 83].

## 9.2. Thermally Modified Starches

### 9.2.1. Instant Starches

*Pregelatinized* starches are precooked products that are cold-water soluble, i.e., they can be used without cooking/heating and will produce dispersions without lumps when correctly prepared [84, 85]. They may be made from either native or chemically modified (Section 9.1) starches by two general methods. In one method, a starch-water slurry is applied to a steam-heated roll or into the nip between two nearly touching and counterrotating steam-heated rolls, where the starch is rapidly gelatinized, pasted, and dried. The dry film is scraped from the roll and milled to

a powder. The resulting product should contain no intact granules, except when the starting material is a highly cross-linked starch. The other way to make a pregelatinized product is to pass a starch and some moisture through an extruder, in which the heat and shear imparted by the process conditions disrupts the granules. In this process also, the dried product is ground to the desired mesh size.

Pregelatinized starch products are used in food and laundry products when (1) no heat for cooking is available, (2) no process step requires sufficient heat to cook the starch, or (3) heat cannot be applied because of the heat liability of one or more of the other ingredients. If modified starches are used in the preparation of the pregelatinized starch product, the properties of the paste introduced by any modification(s) are also exhibited by the pregelatinized product.

Products known as *cold-water-swelling (CWS) starches* contain granules that swell extensively in the presence of ambient temperature water [85]. They are made by two different processes. In one case, a slurry of starch granules in aqueous alcohol is heated to disrupt the internal granule structure, i.e., to gelatinize the granules, without much granule swelling and no dissolution of the polymers. In the other, an aqueous starch slurry is atomized via a special spray-drying nozzle into a stream of heated air. Granules in cold-water-swelling starches are gelatinized, but their granular form is maintained (as opposed to pregelatinized products). Both pregelatinized and CWS starches are categorized industrially as *instant starches*.

Starches that are neither pregelatinized nor cold-water-swelling are known as *cook-up starches*.

### 9.2.2. Annealed and Heat-moisture-treated Starches

While preparation of instant starches is widely practiced, less common are thermal treatments known as *heat-moisture treatments (HMT)* and *annealing* [86]. *Annealing* results from heating granular starch in excess water (> 40%) at a temperature above the glass transition temperature but below the onset temperature of gelatinization. The resulting changes in properties are a function of the parent starch, the treatment tem-

perature, and the duration of heating, but the most common and consistent effects of annealing are increased onset and peak gelatinization temperatures, an increased enthalpy of gelatinization (not always observed), a narrowing of the gelatinization temperature range, and decreased digestibility (Section 5.2 and Chap. 11).

Heat-moisture treatment also involves heating of starch granules above their glass transition temperature, but differs in that it is conducted at reduced levels of moisture (< 35%) and at higher processing temperatures (80–140 °C). The variables in this process are the type of starch, the moisture content of the starch, the treatment temperature, the heat source, and the duration of the treatment. Common property changes are increases in onset, peak, and often conclusion gelatinization temperatures; reduced granule swelling and solubility; reduced leaching of amylose; decreased peak viscosity; increased paste stability; reduced enthalpy of gelatinization (though, in some cases, enthalpy may not change); and decreased digestibility (Section 5.2 and Chap. 11). However, due to the diverse range of treatment conditions and starches utilized for HMT, the resulting starch characteristics and properties can vary considerably.

### 9.2.3. Dry Heating of Starches

Commercial products are made by heating dry starch (< 15% moisture) at a temperature below that at which thermal degradation occurs (90–128 °C) [86]. Products generally exhibit greater stability to the conditions of heat and shear imposed by cooking processes. An increased paste viscosity and a creamy consistency for quick-cooking products are also claimed.

### 9.2.4. Destructurized and Thermoplastic Starch

Although destructurized and pregelatinized could be considered to be synonymous terms (because a pregelatinized starch is destructurized to mixtures of amorphous amylose and amylopectin), the term *destructurized starch* was originally (1987) used to describe starch of relatively low moisture content (10–25%) that was heated under pressure in an extruder to a temperature

above its glass transition and melting temperatures to yield a thermoplastic mass that could be made into a molded article or film. The difference between a pregelatinized starch made by extrusion cooking and a thermoplastic destructured starch is in the amount of moisture used as a plasticizer in the feed and, hence, the temperature needed to melt the starch [87, 88]. Addition of other plasticizers, such as glycerol, allows the starch to be converted into a thermoplastic material at lower moisture contents than are required for traditional starch pasting. Addition of a depolymerizing catalyst to reduce polymer molecular masses gives a product from which shaped articles with improved characteristics can be made.

*Thermoplastic starch* can be blended with natural or synthetic hydrophilic polymers. In some cases, the blends can be further mixed with hydrophobic polymers, such as polyethylene, for production of water-resistant, blown films [82]. Destructured starch can also be mixed with plasticizers and other materials such as natural and synthetic polymers, graft copolymers, and lubricants to produce a large family of products also known as thermoplastic starch. Thermoplastic starch can also be made by esterifying or etherifying (e.g., hydroxypropylating) starch to high DS values (DS 2 or more) [82]. Thermoplastic starch materials can be subjected to various thermoforming processes such as spinning, extrusion, film blowing, injection molding, and foaming. The products are usually biodegradable.

### 9.3. Genetically Modified Starches

The characteristics of native starches can be modified genetically [89]. A major commercial starch that is the base starch for many modified food starch products is *waxy maize starch*, a maize starch devoid of amylose (Chap. 4). Waxy (all-amylopectin) and partial waxy (reduced amylose content) wheat starches, as well as all-amylopectin potato starch have been developed. Rice plants produce starches with a range of amylose contents from less than 1% to at least 33%. Commercial hybrids of corn, known as *high-amylose corn* or *amylo maize starches*, produce starches with ca. 55% and > 70% contents of amylose.

### 9.4. Multiple Modifications of Starches

Starches are modified for many and diverse specific applications (Chap. 10). Variables include choice of the parent starch, including a genetically modified starch (Section 9.3), type of chemical modification (Section 9.1), and any thermal treatment (Section 9.2). Many modified starch products are made by combinations of treatments. As examples, a coating binder starch for a papermaking process will likely be hydroxyethylated (stabilized) and thinned, and a food starch might be made by cross-linking, stabilizing, thinning, and pregelatinizing waxy maize starch (a genetic modification). Major commercial individual (combinations of these modification processes are commonly used) starch modification processes and products are listed below:

#### Chemical reactions

##### A. Cross-linking

1. Esterification (approved for food use)
  - a. Distarch phosphates (approved for food use)
  - b. Distarch adipates (approved for food use)
2. Etherification
  - a. Starch cross-linked by reaction with epichlorohydrin [106-89-8] (not used in foods in the USA)

##### B. Stabilization

1. Etherification
  - a. Hydroxyethylstarches
  - b. Hydroxypropylstarches (approved for food use)
  - c. Cationic starches
  - d. Starch graft copolymers
2. Esterification
  - a. Starch acetates (approved for food use)
  - b. Starch oct-1-enylsuccinates (approved for food use)
  - c. Monostarch phosphates (approved for food use)
3. Oxidation
  - a. With hypochlorite (approved for food use)
  - b. With hydrogen peroxide and Cu(II) ions (approved for food use)
  - c. With ammonium persulfate

##### C. Depolymerization

1. Acid-catalyzed (approved for food use)

2. Oxidation, followed by alkaline pH (approved for food use)

D. *Transglycosylation plus depolymerization (dextrinization)* (approved for food use)

**Physical/thermal transformations**

- A. *Pregelatinization* (approved for food use)
- B. *Preparation of cold-water-swelling starch* (approved for food use)

**Genetic control/plant breeding** (approved for food use)

**10. Examples of Uses of Starches and Products Derived from Starches**

**10.1. Uses of Starches**

The primary uses of starches, which vary from country to country and region to region (see Table 5) [90], are to produce sweeteners (dextrose, glucose syrups, HFS) and related products (maltodextrins, syrup solids), in paper and paperboard product manufacture [91], in processed food preparations [92], and to produce fuel ethanol, although as already mentioned, most ethanol is produced by processes in which the starch is not isolated as a pure material. Some examples of uses of specific products follow, although essentially all products employed in paper manufacture and as a textile sizing agent have been thinned, and many of the products used in the food industry have been pregelatinized and/or

thinned in addition to being both cross-linked and stabilized. Thus, relating a specific modified starch to a specific application is often not possible.

Selected examples of nonfood uses of starches, which term includes both native and modified (derivatized, oxidized, and acid-thinned products, starch-latex copolymers, dextrans, and pregelatinized products) starches are as follows:

- Absorbants
- Briquette binder
- Carpet and rug sizing
- Ceramics (clay binder)
- Fiberglass sizing
- Ink and dye thickeners
- Manufacture of paper, boxboard, corrugated board, fiberboard drums, spiral tubes, etc. (wet-end additive, sizing agent, coating binder, adhesives [remoistenable, case and carton sealing, laminating, tube winding, and bag adhesives])
- Ore refining (both flotation and electrolytic reduction processes)
- Tablet binder and excipient
- Textile finishing and sizing
- Wall-covering pastes

Selected examples of food uses of starches, which term includes both native starches and modified (derivatized [cross-linked and stabilized], oxidized, and acid-thinned products, dextrans, and pregelatinized) products are as follows:

- Baby foods
- Biscuits, crackers, cookies
- Batters and batter mixes
- Beverage emulsions
- Breadings and breading mixes
- Breakfast cereals
- Cake, pancake, doughnut, muffin, and waffle mixes
- Confections (gum, jelly, and panned products)
- Fillings for pies and other baked goods (cream and fruit)
- Glazes
- Gravies and gravy mixes
- Hot-filled products in jars and cans
- Noodles
- Pet foods
- Processed cheese products

**Table 5.** End-use demand for starches in some major markets [90]

	Approximate percent of total use		
	EU	USA	Japan
To produce glucose syrups, dextrose, and maltodextrins	28	12	27
To produce HFS <sup>a</sup>	5	31	27
In processed foods	18	3	21
To produce paper and paperboard	22	10	11
To produce fuel ethanol	2	42	5
Other industrial uses <sup>b</sup>	26	2	10

<sup>a</sup>High-fructose syrups.

<sup>b</sup>Includes textiles, personal care products, chemicals other than ethanol, detergents, pharmaceutical, and other industrial products.

- Processed meat products
- Pudding, pie filling, and other dessert mixes
- Retorted canned products
- Salad dressings (spoonable and pourable)
- Sauces and sauce mixes
- Snack and other extruded foods
- Soups and soup mixes
- Surimi
- Toppings and syrups
- Yogurt

Approximate utilization of corn/maize starch isolated by the wet-milling process in the USA:

**As starch products (ca. 16%) [9]**

- In paper and paperboard manufacture (ca. 10%)
- In processed food products (ca. 3.0%)
- As a textile size (ca. 2.0%)

**As the result of conversion (ca. 85%); excluding that used to produce ethanol [9]**

- As high-fructose syrups (ca. 49%)
- As glucose syrups, dextrose, and maltodextrins (ca. 36%)

Uses of native (i.e., unmodified) starches are limited. In the food industry, they are used to dust molds for jelly-type confections, for moisture control (e.g., in salt), to help dissipate heat during grinding of sugar to produce powdered sugar, and for dusting of marshmallows and chewing gum. Nonfood uses include their use in papermaking, where the papermaker purchases a native starch, then subjects it to controlled oxidative (ammonium persulfate, potassium persulfate, sodium hypochlorite, or hydrogen peroxide) or enzyme-catalyzed ( $\alpha$ -amylase) depolymerization or derivatization on site. Native starch is used to make porous ceramic filters (e.g., for diesel vehicle exhaust) and, with addition of other ingredients, as the adhesive for corrugated board manufacture [93]. Native starches are combined with plasticizers and other additives and pregelatinized/destructurized in an extruder to prepare water-soluble, loose-fill packaging material.

Acid-modified and other thinned products are used in the warp sizing of textiles, as adhesives, and in the manufacture of gypsum and corrugated board [93].

As mentioned, many derivatized starch products are also “thinned.” Those starches that have been thinned, but otherwise unmodified (i.e., thin-boiling or fluidity native starches), are used to make gum candies (e.g., jelly beans, jujubes, orange slices, spearmint leaves) and processed cheese loaves.

*Cross-linked products* are mostly used in the food industry, and food processors use both cross-linked-only products and starches that have been both cross-linked and stabilized (i.e., dually modified). Cross-linked starches are used as thickeners in canned (retorted) and hot-filled products such as sauces, soups, gravies, pie fillings, puddings, spoonable salad dressings, and baby foods and in batter mixes. Cross-linked and stabilized starches are used in preparation acidic food products such as tomato-based sauces, salad dressings, and fruit pie fillings; retorted products such as sauces, soups, and gravies; aseptically-filled products such as puddings and cheese sauces; frozen foods such as pot pies, fruit pies, and gravies; and baby foods.

*Stabilized-only starches* are used in both food and nonfood applications. Starch acetates and hydroxypropylated starches are used as thickeners of food products when low-temperature stability is required (e.g., in chilled and frozen products) and in general when retrogradation/setback is undesirable. The most widely used stabilized starch for nonfood applications is hydroxyethyl starch, which is used in papermaking as a furnish additive, a surface sizing agent, and as a coating and pigment binder [91]. Hydroxyethyl starch also finds use in textile sizing [94]. Acetylated starches are used in surface sizing of certain paper products and for warp sizing of textiles.

*Cationic starches* are used in the papermaking process as a wet-end additive to balance fiber flocculation and retention in order to promote sheet dewatering and to attain good sheet formation and strength [91]. It is also used in surface sizing in certain paper products, and even less often as a coating binder. Cationic starch also finds use as a flocculant for anionic materials and in fabric softeners.

*Monostarch phosphates* find use in both food and nonfood applications. They can be used with alum as a wet-end additive in making paper at low pH. They are also used as flocculants and sedimentation aids for various cationic materials and in textile sizing and printing pastes.

The amphiphilic *octenylsuccinylated starches* are special types of stabilized starch products. These starches are used in emulsion preparation and stabilization in products such as pourable salad dressings and flavored beverages. They are also used to encapsulate certain flavors, aromas and drugs and as fat spacers.

*Carboxymethylated starches* are used as sizing agents for textiles [94]. Higher-DS products are used as additives to control fluid loss and to modify the rheology of drilling muds in oil and natural gas production.

Uses and potential uses of starch graft copolymers have been reviewed [82, 95]. Graft copolymers of starch with a latex are useful as paper-coating materials. Some polyacrylate starch copolymers are employed as super-absorbants.

Pregelatinized starches are widely used. Non-food uses include as a spray-on laundry starch, as an adhesive in foundry cores for metal casting, as a binder, and as an excipient in solid oral dosage forms of pharmaceuticals. Their use in foods is varied and widespread since cross-linked and/or stabilized starches can also be pregelatinized. A common use is in dry mixes for such products as instant puddings and soups. They are also used in pizza toppings, extruded snacks, soft cookies, bakery fillings, and low-fat salad dressings. Cold-water-swelling starches are used to thicken sugar solutions and glucose syrups in the preparation of gum candies, in certain desserts, and in muffin mixes.

Thermoplastic starch can be used to prepare food, lawn, and leaf bags for composting, food-service ware, pharmaceutical capsules, personal hygiene products, and packaging material and as fillers for tires.

## 10.2. Uses of Products derived from Starches via Extensive Depolymerization

The primary uses of dextrins are to prepare adhesives for paper and paperboard products [50], where they are used as bag-seam pastes (white dextrins, British gums), in tube winding (white and yellow dextrins, British gums), for case and carton sealing (white and yellow dextrins), in laminating (white and yellow dextrins,

British gums), in preparation of remoistenable gummed tape and labels (white and yellow dextrins), and in envelope manufacture (white and yellow dextrins).

In the food industry, white dextrins are used in pan coating of confections, as a gloss for bakery products, and as carriers for flavorings, spices, and colorants.

Syrup solids and maltodextrins are utilized in foods in many of the same applications, which include use as agglomerating agents, as binders, as bulking agents, in coatings, as coffee whiteners, in frozen foods, in infant formulas, in meat products, in processed cheese products, and in whipped toppings. Maltodextrins are used to encapsulate flavors and aromas.

Glucose syrups are produced in large quantities and their use is widespread in food products. (Syrup viscosity is important as it relates to the handling characteristics of the syrup and the texture of the food product). They are used largely as humectants and to provide bulk and body with various degrees of sweetness. Products with low sweetness provide body to ice cream, canned fruits and vegetables, bakery products, and some confections. Products with moderate sweetness are used in foods requiring body but not high sweetness (e.g., in sauces, toppings, and some confections) and sweet bakery products. Glucose syrups are used to reduce water activity, lower the freezing point, increase the osmotic pressure, and increase the chewiness of a food product. They also inhibit crystallization of sucrose. In ice cream, they provide resistance to meltdown. They increase the shelf life of hard candies and peanut brittle by preventing crystallization and providing resistance to changes in moisture. They provide fermentable substrates and contribute to browning of bakery products, and are used in many other applications from bakery fillings to salad dressings.

Glucose syrups are the carbon source for a variety of fermentation processes that are used to produce a range of products from lactic acid to antibiotics, and as has already been mentioned, various salts are added to them to produce anti-freeze and deicing solutions.

High-glucose syrups are the starting materials for the production of sorbitol [50-70-4], ascorbic acid (vitamin C) [50-81-7] via sorbitol, glucono- $\delta$ -lactone (D-glucono-1, 5-lactone) [52153-09-0],

and polydextrose [68424-04-4], all of which are widely used in their own rights.

Crystalline D-glucose is used in many of the same products that utilize glucose syrups when a dry form of sugar is desired. In addition, when it is used as part of the sugar coating of doughnuts and in sandwich cookie and sugar wafer fillings, it imparts a desirable cooling sensation in the mouth because of its slight negative heat of solution.

Most often, hydrogenated starch hydrolysates (HSH) are used to make food products for diabetics. Some is also used to make sugarless candies and chewing gum.

High-fructose syrup containing ca. 42% fructose (HFS 42) is used as the sweetener in many fruit-flavored beverages, in doughs used in production of yeast-raised breads and rolls, and in batters used in production of cakes. HFS 42 is blended with sucrose and glucose syrups in fruit canning. Dairy products, namely, chocolate milk, yogurts, milk-based nutrition drinks, ice cream, frozen novelties, and frozen desserts, as well as nondairy products such as jams, fruit fillings, barbecue sauces, and cake frostings, may also contain HFS 42. Most cola drinks are made with HFS 55.

$\beta$ -Cyclodextrin ( $\rightarrow$  Cyclodextrins) is primarily used to prepare powdered essential oils, which are thereby protected from oxygen and light, but which are readily released when the dry powder is added to an aqueous system. Such dry complexes are used in dry mixes for baked goods, beverages, and soups; flavored coffee and tea; savory snacks and crackers; breakfast cereals; chewing gum; tableted candies; processed cheese products; gelatin desserts; and puddings. It is also used to protect other aromas, flavors, and certain pharmaceuticals from oxidation, volatilization, light-induced degradation, and thermally induced decomposition.

## 11. Starch Digestibility

Not all starch is equally digestible. In a food product containing starch, there will be fractions termed *rapidly digestible* (or *rapidly digesting*) starch (RDS), *slowly digestible* (or *slowly digesting*) starch (SDS), and *resistant starch* (RS). Rapidly digesting starch is the fraction which, in a laboratory analysis designed to mimic diges-

tion in the stomach and small intestine, is converted into D-glucose within 20 min. Slowly digestible starch is the fraction that is converted into D-glucose in the time period between 20 and 120 min. Resistant starch is the portion of starch that does not undergo digestion in the small intestine (is not converted into D-glucose within 120 min in the laboratory test). It is fermented by the microflora in the large intestine (colon) and, therefore, falls under the definition of dietary fiber. There are four general classes of resistant starch: *RS1* (starch that is physically inaccessible to the digestive enzyme  $\alpha$ -amylase because it is encased within plant cell walls, nondigested denatured protein, or something else that entraps it); *RS2* (uncooked, i.e., ungelatinized granular starch); *RS3* (retrograded starch in which starch polymer molecules [primarily amylose molecules] are highly associated and attacked by  $\alpha$ -amylase only slowly); and *RS4* (granules that are resistant to the action of  $\alpha$ -amylase because of chemical modification). The glycemic index of the fractions is RDS > SDS > RS.

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