

Modification of Starches

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I. Introduction

Starches are inherently unsuitable for most applications and, therefore, must be modified chemically and/or physically to enhance their positive attributes and/or to minimize their defects. Starch derivatives are used in food products as thickeners, gelling agents and encapsulating agents, in papermaking as wet-end additives for dry strength, surface sizes and coating binders, as adhesives (corrugating, bag, bottle labeling, laminating, cigarettes [tipping, side-seam], envelopes, tube-winding and wallpaper pastes), for warp sizing of textiles, and for glass fiber sizing. Various starch products are used to control fluid loss in subterranean drilling, workover and completion fluids (for oil, gas or water production). Modified starches are also used

in tableting and cosmetic formulations. Some starch is incorporated into plastics to enhance environmental fragmentation and degradation. Thermoplastic starch and starch-polymer composites can replace petroleum-based plastics in some applications. Newer applications include use of nondigestible starch as nutraceuticals. The future of starch may include a role in detergents.

The properties required for a particular application, availability of the starch and economics play a role in selecting a particular native starch for subsequent chemical and/or physical modification. Normal maize, waxy maize, high-amylose maize, tapioca, potato and wheat starch are the most available and accessible starches, but varieties of rice, including waxy rice, pea (smooth and wrinkled), sago, oat, barley, rye, amaranth, sweet potato and certain other exotic starches indigenous to the areas in which they are produced can be used as localized commercial sources. Conventional hybrid breeding and genetic engineering has the potential to provide even more options.¹⁻⁴

Chemical modification of starch generally involves esterification, etherification or oxidation of the available hydroxyl groups on the α -D-glucopyranosyl units that make up the starch polymers.¹ Reactions used to produce most commercially-modified starches have been reviewed by others.^{5,6} Many commercial derivatives are produced by the addition of reactive, organic reagents to aqueous starch slurries while controlling alkalinity (pH 7-9 for esterification and pH 11-12 for etherification) and temperature (typically $<60^{\circ}\text{C}$). Sodium sulfate or sodium chloride is often added to restrict swelling of the starch granules during reaction. Neutralization of the reaction slurry, typically by hydrochloric or sulfuric acid, followed by water washing of the filter cake and drying, yields a powder. Generally, the degree of substitution (DS) of commercial starches is less than 0.2. Dry or semi-dry reactions and reactions in ethanol or isopropanol slurries are known. While these methods allow higher substitution, salts and modifying reagent by-products remain in the final product. A continuous method of hydroxypropylation in a static mixer reactor has been described.^{7,8} Another process involves the use of a cylindrical turbo-reactor for etherification, esterification and acid modification.⁹ A stirred, vibrating, fluidized-bed reactor for

¹Editor's note: Starch modification was reviewed and discussed in the first edition of this work, viz., H.J. Roberts, *Nondegradative Reactions of Starch*, in Vol. I, 1st edn, 1965, pp. 439-493; P. Schildneck and C.E. Smith, *Production and Use of Acid-modified Starch*, in Vol. II, 1st edn, 1967, pp. 217-235; B.L. Scallet and E.A. Sowell, *Production and Use of Hypochlorite - Oxidized Starches*, in Vol. II, 1st edn, 1967, pp. 237-251; R.B. Evans and O.B. Wurzburg, *Production and Use of Starch Dextrins*, in Vol. II, 1st edn, 1967, pp. 254-278; J.W. Knight, in *Modification and Uses of Wheat Starch*, in Vol. II, 1st edn, 1967, pp. 279-291; H.J. Roberts, *Starch Derivatives*, in Vol. II, 1st edn, 1967, pp. 293-350; R.M. Hamilton and E.F. Paschall, *Production and Use of Starch Phosphates*, in Vol. II, 1st edn, 1967, pp. 351-368; L.H. Kruger and M.W. Rutenberg, *Production and Uses of Starch Acetates*, in Vol. II, 1st edn, 1967, pp. 369-401; E.F. Paschall, *Production and Use of Cationic Starches*, in Vol. II, 1st edn, 1967, pp. 403-422; E.T. Hjermstad, *Production and Use of Hydroxyethylstarch*, in Vol. II, 1st edn, 1967, pp. 423-432; C.H. Hullinger, *Production and Use of Cross-linked Starch*, in Vol. II, 1st edn, 1967, pp. 445-450; and in other chapters in Volumes I and II such as those on specific starches and starch applications in the food, paper, and textile industries. The subject was updated in the 2nd edition, M.W. Rutenberg and D. Solarek, *Starch Derivatives: Production and Uses*, 2nd edn, 1984, pp. 311-388; R.G. Rohwer and R.E. Klem, *Acid-modified Starch: Production and Uses*, in 2nd edn, 1984, pp. 529-541; and again in chapters on specific starches and starch applications. This chapter covers primarily the patent literature from the early 1980s through part of 1998. An additional update can be found in K.C. Huber and J.N. BeMiller, *Modified Starch*, in 'Starch and Other Biopolymers', A. Bertolini, ed., Taylor and Francis/CRC Press, in press.

modifying starch with gaseous ethylene oxide has been described.¹⁰ Reactive extrusion to prepare starch succinates has been studied.¹¹ An extrusion process for preparing crosslinked, carboxymethylstarches as water absorbents has been developed.¹²

Unless some insolubilizing, crosslinking treatment or a hydrophobic substituent is added, increasing substitution will eventually make the starch cold-water-soluble. Steric consequences of substituent groups bring about the disruption of hydrogen bonding and weakening of the granular structure.¹³ Anything that breaks glycosidic linkages, e.g. thinning under acidic conditions or oxidation under alkaline conditions, also weakens the granular structure.

Monofunctional reagents provide nonionic, cationic, anionic and hydrophobic or covalently reactive substituent groups that dramatically affect the properties of the particular starch being modified. The type of modification alters the gelatinization temperature and pasting characteristics of the starch and stabilizes the paste resulting from cooking a suspension by controlling or blocking associations between dissolved amylose and amylopectin molecules. Such so-called stabilizing modifications result in improved freeze-thaw and refrigerated storage stability, an important property for food systems. Differential scanning calorimetry (DSC), which measures the energy needed to disrupt recrystallized or retrograded starch after low temperature storage or repeated freeze-thaw cycles, has provided evidence that chemical modification reduces or eliminates aggregation and/or association of starch molecules during cold storage of pastes.¹⁴

Hydroxypropylstarches prepared by etherification with propylene oxide and starch acetates prepared by esterification with acetic anhydride are commonly used in food applications. Enhanced stability is achieved by using an all-amylopectin starch, e.g. waxy maize starch. Hydroxypropylation is more effective than acetylation in imparting low temperature stability. Similar reduced-retrogradation properties are provided by hydroxyethylation with ethylene oxide, but this modification is not permitted in food applications. Chemical modification provides improved stability and film-forming properties to partially-degraded starches used in paper surface sizing or coating, textile warp sizing and adhesives. In food applications, these modifications can be combined with crosslinking treatments to provide a range of products with a range of properties. Starch and modified starch for food applications has been reviewed.¹⁵

Difunctional reagents are capable of crosslinking starch polymers by reacting with more than one hydroxyl group and, thereby, reinforcing granules. The most common crosslinking agents for food applications are phosphoryl chloride (phosphorus oxychloride), adipic-acetic mixed anhydride and sodium trimetaphosphate. Epichlorohydrin may be used for industrial applications. The stability of the crosslinks provided by these respective reagents varies. The adipate diester crosslink is the most labile, particularly at higher pH. Crosslinking restricts swelling of starch granules and the solubility and mobility of the polymer molecules. Pastes of lightly crosslinked starches (1×10^{-3} to 5×10^{-2} percent of crosslinking reagent based on the weight of starch) have shorter textures, higher viscosity, greater resistance to shear-thinning and low pH, and overall greater stability than the native starch from which they are made. Covalent crosslinking partially compensates for the hydrolysis of the starch molecules that may occur at low pH. More highly crosslinked starches (>0.5% reagent) will not gelatinize in boiling water or under sterilization conditions¹⁵

and are typically used in dusting powder applications. Crosslinking of dispersed or swollen starch can be used to improve the water resistance of starch films; for example, acetone-formaldehyde condensates are used in starch-based corrugating adhesives. It has been reported that crosslinking of amylose-containing corn and potato starch granules joins amylose molecules to amylopectin molecules.¹⁶

Starch polymers are often partially depolymerized to produce products that generate less viscosity on cooking a unit weight of starch; such products are known as fluidity or thinned starches. Depolymerization may be effected by an acid or an oxidant. Such treatment is generally carried out on granular starch. Fluidity (thinned) starches result from treatment of a slurry of granular starch with dilute hydrochloric or sulfuric acid at 40–60°C. Dextrins are more highly degraded and are produced by heating dry acidified starch at 100–200°C. Some transglycosylation also occurs in this process, resulting in more highly branched polymer molecules. Acid-catalyzed hydrolysis of potato, high-amylose maize and waxy maize starches in aqueous methanol, ethanol, isopropanol, butanol and blends of alcohols has been examined.¹⁷ A wide range of limit dextrins with specific DP values were produced using 0.36–5.0% hydrochloric acid at 5–65°C. It was proposed that crystalline regions in the starch granules were converted to amorphous regions during this hydrolysis.¹⁸ Acid conversion of non-crosslinked starch esters or ethers in aqueous ethanol (6 weight percent water) at 50–150°C and under pressure produced degraded, cold-water-soluble starches.¹⁹ Suggested applications for the products, which formed clear, transparent films, were for wall covering and other remoistenable adhesives, protective colloids for emulsion polymerization and encapsulation. Starch polymers can also be depolymerized using various enzymes (amylases). These conversions are typically done on cooked (pasted) starch and typically to a much greater degree, i.e. to produce D-glucose and/or malto-oligosaccharides.

II. Cationic Starches

Cationic starches have significant use in papermaking as wet-end additives for dry strength, as emulsion stabilizers for internal, synthetic sizing agents, such as alkyl ketene dimer and alkenyl succinic anhydride, and as surface sizing agents^{20,21} (see also Chapter 18). In recent years, much work has been done to develop synergistic, wet-end additive systems with inorganic microparticles (colloidal silica, bentonite) and/or synthetic polymers or even other starches. The goal is improved retention of cellulose fines and filler, better sheet formation, enhanced drainage and greater strength. Overall, cationic starches provide both wet and dry strength in the final paper.

Quaternary ammonium cationic starch prepared by treatment with 2,3-epoxypropyltrimethylammonium chloride or the more stable chlorohydrin form (3-chloro-2-hydroxypropyltrimethylammonium chloride, which is converted to the reactive epoxide under the highly alkaline starch reaction conditions) is the major commercial cationic starch type. Quaternary ammonium cationizing reagents where one of the methyl groups is replaced with a hydrophobic group (e.g. dodecyl, cocoalkyl or octadecyldecyl) have been examined. Polysaccharides modified with them have enhanced thickening properties.²²

Many products contain 0.1–0.4% nitrogen (<0.05 DS), but more highly substituted products accessible from dry cationization are available. Germany allows the use of starch products with up to 1.6% nitrogen from reaction with 2,3-epoxypropyltrimethylammonium chloride. A petition has been filed with the US Food and Drug Administration that proposes that 2,3-epoxypropyltrimethylammonium chloride be allowed in food-contact articles.²³ The current allowable level is 5%.

Tertiary amino starches made by etherification with diethylaminoethylchloride are also available. Protonation of the tertiary amine under acidic pH conditions produces the cationic charge, which diminishes as pH increases. The nature of the alkyl groups influences the pK_a of the tertiary amino group. Starches modified with 2-chloroethylmorpholine are useful additives for immobilizing paper coating compositions.²⁴ At pH 8.0–8.5, typical of many coating formulations, the morpholinoethyl substituent is not protonated, but during the process of applying the coating heat can drive off ammonia, causing a drop in pH, protonation (cationization) of the morpholinoethyl group, and flocculation of the pigment, which immobilizes the coating on the paper surface, improving surface properties.

An improvement to slurry cationization involved inline mixing of a solution of commercial 65% 3-chloro-2-hydroxypropyltrimethylammonium chloride with a 21% sodium hydroxide solution to convert the reagent rapidly to the reactive epoxide form just prior to addition to the starch slurry. This process results in less dilution and increased reaction kettle capacity.²⁵ In another process for which greater reaction efficiency was claimed, the chlorohydrin is added to a dilute aqueous caustic solution followed by the addition of starch, small amounts of sodium sulfate and finally calcium oxide to maintain the pH at 11.5–11.9.²⁶ Use of potassium rather than sodium hydroxide to catalyze reactions with the epoxide is claimed to provide higher nitrogen contents.²⁷ Reaction with the usual cationizing reagents on starch dispersions cooked at a high temperature to make cationic²⁸ or amphoteric²⁹ (via combined treatment with sodium trimetaphosphate) starches may be used for on-site derivatization. Countercurrent washing in hydrocyclones can be used to replace the chloride counterions of quaternary ammonium starches with other anions.³⁰

Although cationic corn, tapioca, wheat and potato starches are the most common commercial products, preparations, properties and performance of cationic oat³¹ and pea³² starches have been reported. Improved retention performance via the use of a blend of cationic cereal (wheat, corn) starch and cationic potato starch has been reported.³³ Products for papermaking using all-amylopectin potato starch have been proposed.^{34–39}

1. Dry or Solvent Cationization

Cationization of starch by dry reaction with 2,3-epoxypropyltrimethylammonium chloride is a commercially significant process. The key to a dry reaction is an intimate, homogenous mixture of the reagent and the catalyst. One process^{38,39} describes an ‘activator’ consisting of spray dried, precipitated silica with a surface area of 190 m²/g (BET) that contains an alkaline agent such as calcium oxide or calcium hydroxide and/or silicates. Different ratios of silica to alkali and 1–3% catalyst (based

on dry starch) were used. The viscosity of the final starch product varied based on the nature and the amount of the catalyst. Use of 0.5% 3-chloro-2-hydroxypropyldimethylethanolamine based on the weight of epoxide or halohydrin was claimed to provide high viscosity in the final starch products. More importantly, reaction efficiencies of 90–95% (versus 70–85% for aqueous reactions) and higher DS values of 0.2–0.5 (versus 0.05–0.06) are possible.⁴⁰ With intensive mixing of reactants, complete cationization can occur in storage hoppers, silos or bags at ambient temperature. This feature depends on the reactivity of the particular reagent used rather than the process; other reagents may require a higher temperature for reaction. While the cationic modification is usually complete in 2–3 days, up to 7 days may be required to ensure residual epoxide is <100 ppm.⁴⁰ An extension of this process incorporates up to 1% of a mixture of sodium peroxodisulfate and sodium peroxocarbonate (1:2 to 1:4 w/w) to prepare ‘adjustable viscosity’ cationic starches.⁴¹ Equipment was described for continuously preheating a mixture of starch and the cationizing reagent while maintaining the moisture content to achieve faster reaction.⁴²

Aluminosilicate clays (kaolinite) with a cation exchange capacity of 2.2 meq/100 g were blended with calcium oxide and starch prior to spray addition of the epoxide. The reaction proceeded at ambient temperature without mixing. Greater reaction efficiencies are claimed.⁴³

Salts and organic by-products, mostly the diol resulting from hydrolysis of the epoxide, from dry cationization are left in the starch. Trimethylamine, if formed, can be detected by its odor. It can be neutralized by subsequent addition of acid. Addition of a slightly soluble organic acid, such as fumaric or adipic acid, during the cationization both eliminates the odor and aids scale control in starch cooking equipment.⁴⁴

Cationization and carboxymethylation of starch in an extruder has been reported.^{45–47} Cationization of potato starch in a twin-screw extruder had an optimum reaction efficiency of 71%. Further work yielded 80% efficiency and products with 0.03–0.10 DS.⁴⁴ Additional heat treatment of extruded products (made via reaction with quaternary ammonium reagents) with sodium trimetaphosphate or citric acid has improved reaction efficiencies and/or viscosities.⁴⁸ Dry cationization in the presence of methanol and isopropanol⁴⁹ or combined with microwave irradiation has also been done.⁵⁰

Cationization of waxy maize, corn and barley starches in aqueous alcohol slurries is most effective at 35–65% ethanol for all starch types; a 1:1 starch to water ratio gave highest DS values.⁵¹ A process for making cationic or amphoteric starches in aqueous, alkaline alcoholic solvents has also been described.⁵²

2. Polycationic Starches

It is possible to etherify starch with reagents containing two or more cationic groups (perhaps containing combinations of quaternary, tertiary and/or secondary amines).^{53,54} A typical reagent is 1,3-bis(dimethylamino)-2-chloropropane.⁵³ Such derivatives gave improved drainage, retention and paper strength. A diquaternary cationizing reagent was prepared by the reaction of 3-chloro-2-hydroxypropyltrimethylammonium chloride with dimethylethanolamine to form a dicationic alcohol, which was then reacted with epichlorohydrin.⁵⁴

Products that provide high dry strength in paper and paperboard can be prepared by co-cooking or heating solubilized potato starch with cationic polymers consisting of co-polymerized units of diallyldimethylammonium chloride, *N*-vinylamine (from hydrolyzed *N*-vinylformamide) or *N*-vinylimidazoline.⁵⁵ Usually, 8–12% of the cationic polymer on the weight of starch is used. Complete disruption of the starch granules is required for optimum dry breaking length and burst strength.⁵⁶ Enzymically degraded potato, wheat, corn, rice or tapioca starch cooked or heated with 5–15% of the polymers mentioned above increased retention onto the fibers and dry strength.⁵⁷ Finally, cationic starch graft polymers can be prepared by co-polymerizing degraded and/or modified starches with *N*-vinylformamide and vinyl acetate followed by hydrolysis.⁵⁸ The graft polymers, which contain amino and vinyl alcohol functionalities, are useful as dry and wet strength agents for paper and paperboard. Complexes of oxidized, carboxymethylated starch and poly(dimethyldiallylammonium chloride) have been proposed as binders for papermaking.⁵⁹

3. Amphoteric Starch or Starch-containing Systems

Control of electrostatic interactions between the various components (cellulose fines and fibers, fillers, pigments, inorganic and natural or synthetic polymeric additives) is essential to papermaking (see Chapter 18). Amphoteric starches containing cationic tertiary amino or quaternary ammonium groups and anionic phosphate groups can interact with both anionic and cationic components. Starches containing at least 0.12% phosphorus, prepared under conditions that preserve high molecular weight, give improved drainage efficiency while providing retention and dry strength.⁶⁰ Amphoteric starches can also be prepared via reaction of cationic starch with 2-chloroethylaminodipropionic acid.⁶¹ The amino-dicarboxylate substituent is zwitterionic. Amphoteric potato starch made in this way gave significantly greater retention of fines and filler (CaCO_3) than the base cationic potato starch control in a microparticle-containing, alkaline papermaking system. Starches modified only with these groups also functioned in a paper furnish. This potato starch derivative has found commercial application as a thickener/emulsion stabilizer in cosmetic formulations, particularly in low pH systems.⁶²

Use of multi-component systems can have synergistic effects. This usually involves oppositely charge polyelectrolytes that interact.⁶³ Sequential addition of cationic and a non-phosphorylated anionic starch provided improved retention and drainage. Typically, cationic potato starch and potato starch sulfosuccinate (0.05 DS) are used.⁶⁴ A further process uses anionic (e.g. phosphorylated, oxidized or carboxymethylated) starch and a high molecular weight cationic (usually synthetic) polymer to neutralize the pulp slurry and insolubilize the starch. Swollen starch can also be a component in the system. The separately added polymers improve concolor, ring crush and burst strength.⁶⁵ An amphoteric combination was created by partially swelling cationic starch in the presence of 2–3% (based on the weight of starch) 0.7 DS carboxymethylcellulose (CMC). This mixture was then added to a filler slurry (e.g. CaCO_3), followed by an inorganic microparticle which has a positive effect on the flocculated mixture, magnesium polyaluminum citrate complex being preferred.⁶⁶

The treated filler slurry is finally mixed with a pulp slurry. Improved sheet properties are claimed. Yet another process involves separate addition of anionic gums and cationic starch to a papermaking furnish to achieve higher dry strength.⁶⁷ Amphoteric starch complexes prepared by co-cooking blends of cationic and anionic starch can also be used for paper and paperboard manufacture.^{68,69} Tapioca starch modified with 3-chloro-2-hydroxypropyldimethylbenzylammonium chloride, propylene oxide and sodium hypochlorite is useful in stabilizing emulsions used in paper sizing.⁷⁰ Similarly, a blend of cationic corn starch and tapioca starch modified with an alkylsuccinic anhydride,⁷¹ complexes of tertiary amino cationic corn starch and sodium poly(acrylate), complexes of quaternary ammonium tapioca starch and poly(styrene sulfonate)^{72,73} and degraded, high DS (0.5–1.0) cationic starches⁷⁴ can be used in the preparation of stable alkylketene dimer emulsions for paper sizing.

Combinations of cationic starch and anionic microparticles are useful commercial systems. Shear-sensitive flocculation occurs, allowing microscale reflocculation in the formed paper sheet, which improves dewatering and retention.^{63,75,76} The microparticles can be colloidal silica, aluminum silicate, poly(silicic acid) or bentonite of specific size and surface area.^{77–79} Cationic, anionic or polymeric aluminum-containing compounds can be additional components. A three-part coacervate system uses a high molecular weight anionic polyacrylamide, cationic starch and silica.⁸⁰ Cooking cationic starch in the presence of an anionic silica hydrosol was reported to improve drainage and retention.⁸¹

A different approach⁸² uses sodium polysilicate microgels to prepare ‘silicated cationic starch.’⁸² The polysilicate is mixed with an aqueous cationic starch slurry at pH 10.4–10.8. Sodium sulfate may be present to control swelling of the starch granules and deposition of the polysilicate. The reaction is completed by acidification to less than pH 6.5. Products with 5–20% microgels are obtained. Analysis indicated some orthosilicate bonding. Improved drainage and fines retention over the typical two-component system (cationic potato starch and silica) was claimed. The polysilicate microgels and cationic starch can also be added separately.^{82,83}

Controlled crosslinking of cationic starches improves performance in microparticle-containing papermaking systems.^{84–86} Superior performance over cationic potato starch was achieved with crosslinked cationic or amphoteric waxy maize, tapioca or potato starch in microparticle systems when the starch cooking was optimized to produce the proper colloidal dispersions.⁸⁶

4. Cationic Starches with Covalently-reactive Groups

Temporary wet strength is desirable in toweling or tissue that may be disposed of in septic systems and for applications where water resistance is needed only for short periods. Dialdehyde starch (DAS) is a good temporary wet strength agent.^{87,88} Reaction of the aldehyde groups of DAS with the hydroxyl groups of cellulose creates a reversible, hemiacetal-bonded network that provides initial wet strength. DAS is prepared by treatment of starch with periodate (IO₄) which selectively oxidizes the adjacent hydroxyl groups on C-2 and C-3 of the α -D-glucopyranosyl units. Intra- or intermolecular reactions of the aldehyde groups produce a highly crosslinked structure

within the starch itself.⁸⁹ Controlled degradation of DAS by heating it in mildly alkaline or acidic water results in complete dispersion of the starch and regeneration of the aldehyde groups.⁸⁸ Due to its degraded structure, a large number of reactive groups are needed for efficient crosslinking. Generally, products with 50–90% oxidation are best.⁹⁰ The process for making DAS requires electrolytic oxidation of the spent oxidant, iodate (IO_3), back to periodate.⁹¹ An improved process for electrochemical regeneration of the periodate has been suggested.^{92,93} Products with 40–65% oxidation appear to give the best balance of material consumption, reaction time and properties.

Reacting cationic starch with *N*-(2,2-dimethoxyethyl)-*N*-methylchloracetamide introduces acetal substituent groups. Cationic starch aldehydes can be generated from this product by cooking the starch at low pH just prior to use in the papermaking system.⁹⁴ Commercial products with less than 1% aldehyde functionality yielded superior wet-strength performance in tissue paper compared to cationic DAS, and higher dry strength than either DAS or conventional cationic starches.⁹⁵ As when DAS is used, the wet strength is temporary. Improved paper machine runability and sheet properties were obtained when the cationic starch aldehyde was used in line paper systems.⁹⁶ Cationic starch or maltodextrin can be esterified with *cis*-1,2,3,6-tetrahydrophthalic acid by heating a dried mixture of the carbohydrate and reagent. Subsequent oxidation of the ester substituent with ozone generates aldehydes (preferred products have 1.0 DS).⁹⁷

Starches containing reactive silanol substituents were prepared by treatment with glycidoxypropyltrimethoxysilane. Under alkaline etherification reactions, the methoxyl groups are removed forming the silanol.⁹⁸ The starch products have good adhesion to glass. High amylose corn and potato starch derivatives are useful binders for glass filaments and facilitate their movement through the various processing steps. Cationic starches modified with silanol groups yielded higher dry strength than did typical cationic starches. The anionic nature of the silanol groups combined with the cationic modification provides amphoteric characteristics. The covalent reactivity of starch silanols with cellulose or starch hydroxyl groups creates networks that provide wet strength.

2-Nitroalkyl ethers are formed by reaction of starch with nitroalkenes generated *in situ* from α -nitro- β -acyloxy (or halogeno) alkanes, such as (2-nitropropyl)acetate, during alkaline slurry reactions at pH 10.⁹⁹ There is some evidence that the nitro group can be reduced with sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) to the primary amine. This treatment can be combined with cationic or anionic modification to give products claimed to be useful in papermaking, adhesives and oil-well drilling.

III. Starch Graft Polymers (See Also Chapter 19)

Starches (particularly hydroxyethylated starches) are commonly used as pigment binders in paper coating formulations (see Chapter 18). Starch binds pigment particles together and to the paper surface, and contributes to water retention in the coating. Starch graft polymers with 1,3-butadiene and styrene appear to produce paper with high gloss and smoothness while maintaining high porosity and ink receptivity.^{100,101} The preferred compositions require enzyme-converted, lightly oxidized hydroxyethylstarch. Thinning is claimed to improve grafting efficiency. Reaction

with a blend of styrene and 1,3-butadiene monomers is carried out under pressure. Ratios by weight of monomer to starch of between 6:10 and 8:10 are suggested. Persulfate or $\text{Fe}^{++}/\text{H}_2\text{O}_2$ are preferred initiators. Surfactants may be used. Films of the starch graft polymers or blends of degraded starches (or other appropriate water-soluble polymers) and latex dispersions have improved coating properties.^{102,103} Films consist of a continuous, water-soluble polymer phase reinforced with non-coalesced, submicron-sized latex particles that provide toughness and mechanical strength. The water-insoluble polymer particles help absorb shrinkage stresses and ensure a smooth, uniform surface. Film continuity translates to more uniform surface wettability in paper coatings. Coalescence of latex particles in conventional coatings can result in surface variations leading to binder migration and the printing defect called mottle.¹⁰³ The improved compositions can be spray dried and subsequently redispersed to yield coatings with good performance. Starch graft copolymers with 1,3-butadiene styrene and optionally acrylonitrile and acrylic acid (as well as other monomers) require use of a dextrin, either a modified or an unmodified one.¹⁰⁴ Use of cationic and/or hydrophobically modified dextrans in emulsion copolymerization has been evaluated.^{105–107} High solids, small particle size and water resistance are claimed properties. Hydrogen peroxide-oxidized or enzyme-degraded potato starch has been graft-copolymerized with styrene-butadiene-acrylic acid or vinyl acetate-butylacrylate and used in moisture-barrier coatings for paper.¹⁰⁸ Paper sacks made with the starch graft polymers had improved repulpability.

Enzyme-thinned cationic starch grafted with vinyl acetate can replace soy protein or casein in board coatings.¹⁰⁹ Enhanced strength and glueability are proposed benefits. Adhesives can be prepared by extruding starch and polymer dispersions, e.g. hydroxypropylstarch and poly(vinyl acetate).¹¹⁰ Starch-based, non-formaldehyde, self-crosslinking binders for nonwovens have also been prepared.¹¹¹ Latexes prepared from maltodextrins (DE <10) polymerized with various acrylate monomers provide high surface tension so that the emulsion stays on the surface of the substrate and inhibits wicking or rewetting. Such starch grafts are subsequently mixed with additional granular starch derivatives and crosslinked by cooking the blend with a cyclic urea-glyoxal condensate. The granular starch, typically a derivative such as hydroxyethylated potato starch, provides film strength. The crosslinker provides water resistance and improved emulsion stability.

IV. Oxidation of Starch

Development or improvement of catalyzed oxidation processes for carbohydrates has resulted in better control, faster reaction rates and higher selectivity. For example, use of small amounts of hydrogen peroxide with 50 ppm of potassium permanganate provides a mild, reproducible starch degradation system.¹¹² The oxidation is done on an aqueous starch slurry at pH 11.4–12.0 at ambient or slightly elevated temperatures. Reaction times are much shorter than those with uncatalyzed hydrogen peroxide. Successive additions of hydrogen peroxide can be made to achieve specific amounts of degradation.

Interest in detergent products derived from renewable resources and with better biodegradability has driven evaluation of oxidized sugars and starches as builders or co-builders in detergents.¹¹³ Builders and co-builders complex calcium and magnesium ions in hard water to prevent scaling or deposits due to precipitation of insoluble carbonate salts. In current powder detergents, the builders are usually zeolites used in combination with polycarboxylate polymers derived from synthetic acrylic-maleic acid copolymers.¹¹⁴

Oxidation of carbohydrates to carboxyl-containing materials is a logical approach to more biodegradable materials.^{115–117} Maltodextrins oxidized under alkaline conditions with oxygen followed by bleaching with hydrogen peroxide yield poly-(hydroxycarboxylic acid) mixtures useful as builders, paper binders and thickening agents.¹¹⁸

Dinitrogen tetroxide (N₂O₄) selectively oxidizes some of the primary hydroxyl groups. One solvent-based process involves selective oxidation of starch with N₂O₄ in the presence of oxygen¹¹⁹ to give a product with 75% uronic acid units. Co-builders for use with zeolites have been produced by oxidation and hydrolysis of starch with a gas phase of NO₂/N₂O₄ in a fluidized bed.¹²⁰

A two step process for producing a dicarboxyl starch derivative uses periodate oxidation to generate dialdehyde starch (DAS) followed by further oxidation with sodium chlorite and hydrogen peroxide.^{121,122} Hydrogen peroxide destroys the by-product sodium hypochlorite. Without hydrogen peroxide, the hypochlorite reacts with chlorite, forming toxic chlorine dioxide and generating a requirement for higher amounts of sodium chlorite.^{115,116}



Dicarboxyl starch can also be made by oxidation with sodium hypochlorite or hypobromite (see reference 116). Reaction with hypochlorite is accelerated by use of catalytic amounts of sodium bromide.^{123,124}

Incorporation of catalytic amounts of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) into the sodium hypochlorite–sodium bromide oxidation system creates a nitrosonium ion that is highly selective as an oxidant for primary hydroxyl groups of carbohydrates.^{125–128} The hydroxymethyl group is selectively oxidized to a carboxyl group via the aldehyde (hydrate) intermediate. Optimum reaction pH is 9.2–9.7 and lower temperatures (0–5°C) are preferred. Although the reaction is faster at pH 10–11,¹²⁷ β-elimination, presumably due to a steady-state aldehyde concentration, is also favored at higher pH values, resulting in degradation of the polysaccharide chain.¹²⁸ At lower pH values the reaction is slower and less selective, and oxidative degradation occurs.¹²⁹ *In situ* formation of sodium hypobromite oxidizes the hydroxylamine back to the active nitrosonium ion.

The TEMPO – sodium hypochlorite – sodium bromide system has been applied to starch ether derivatives, particularly hydroxyethyl starch, which has a primary hydroxyl group on the hydroxyethyl ether group that can also be oxidized to a carboxyl group and carboxymethyl starch. The apparent goal was improved sequestering agents via higher carboxyl content and the proper multidentate conformations

(in which ether oxygen atoms can participate).¹³⁰ A conventional use of sodium hypochlorite is to remove residual protein in starch slurries for absorbable dusting powder applications.¹³¹

V. Starch-based Plastics (See Also Chapter 19)

Problems associated with handling and disposal of solid waste and interest in environmentally-friendly products has created a significant market opportunity for starch.^{132–135} The goal has been to increase the amount of starch in thermoplastic composites designed for various packaging materials, containers and one-time-use, shaped articles prepared by injection molding, blow molding, extrusion, co-extrusion or compression molding.^{136–140}

Use of granular starch as a filler to enhance biodegradation of commodity plastics, such as conventional and linear low density polyethylene and high density polyethylene, polypropylene and polystyrene has been established.^{141,142} Typically, corn starch granules are surface treated with silanes to improve compatibility with the hydrophobic, plastic matrix. An improved process involves the use of starch with a thermoplastic elastomer that functions as a compatibilizer and pro-oxidant.¹⁴³ The starch must be dried to <1% moisture to retard steam formation during extrusion processing. Normal corn starch processed in this way has a density of 1.28 g/cm³ and a particle size of 15 μm and is stable to 230°C. The usual starch content of the product is 6–20%. In addition to increasing biodegradability, starch filler has other claimed benefits: antiblocking, improved printability, improved water vapor permeability, low gloss finish in films; increased dimensional stability in injection molding; and increased stiffness in blow molding.^{132,141} Smaller granules, such as those of rice starch, may be required for very thin films. Starch octenylsuccinate ionically crosslinked with aluminum sulfate can be used as a filler for linear, low density polyethylene (LLDPE). LLDPE-starch octenylsuccinate films had higher strength than did LLDPE-unmodified corn starch films, but a lower degree of biodegradation.¹⁴⁴ Granular corn starch modified with N-methylolstearamide proved to be useful for blending with LDPE.¹⁴⁵

Granular starch and copolymers of ethylene and acrylic esters and alkyl(meth)acrylates or vinylacetate are produced as master batches for the production of mulch films, geotextiles and molded articles.¹⁴⁶ The polar copolymers act as compatibilizers by lowering the interfacial energy between starch and the polyolefin and eliminate the need to coat granules. Processing via a vented twin-screw extruder also eliminates the need for anhydrous starch.

The drive to use starch at higher addition levels requires it to contribute to the expected strength properties. For this to happen, the starch must be disrupted or 'destructured' so that it can form a continuous phase in an extruded matrix. This can be done by extrusion of starch under low moisture conditions, which effects granular fragmentation, melting of hydrogen-bonded crystallites and partial depolymerization. Thermoplastic blends of up to 50% starch and poly(ethylene-co-acrylic acid) (EAA) were produced in the presence of aqueous base, which solubilized EAA and increased its compatibility with starch and urea, which aids in starch gelatinization.^{147,148}

Extrusion blown films containing 40% starch are uniform, flexible and transparent, and have good physical properties. Polyethylene can partially replace EAA to reduce raw material costs and provide improved properties. EAA forms V-type inclusion complexes with both amylose and amylopectin.^{149,150} Jet-cooking EAA-normal starch slurry blends produced higher paste viscosities and different gel strengths (compared to starch pastes prepared without EAA).¹⁵¹ Gel strengths of high-amylose corn starches were decreased with EAA, while waxy maize starch produced uncharacteristically firm gels in the presence of EAA.

Starch composites are formed with poly(ethylene-co-vinyl alcohol) and/or EAA and poly(vinyl alcohol) or another plasticizer, all components being hydrogen bond formers. Three phases, viz., destructured starch with a particle size of <1 micron, synthetic polymer and starch physically or chemically interacted with the polymer, are uniformly dispersed in an interpenetrating polymer network.^{152–157} The mechanical properties of molded articles or films produced from these composites are between those of low density and high density polyethylene.¹³² Breathable, water-impermeable, biodegradable, flexible films useful as backsheets for diapers, protective garments and other articles have been prepared using blends of polycaprolactone and a starch-ethylene copolymer blend made by the above process.¹⁵⁸

Another proposed process employed injection molding in which starch and limited amounts of plasticizing water are heated under pressure to temperatures above the T_g and T_m to transform the native starch into a homogenous, destructured, thermoplastic melt. The process melt is then cooled to below the T_g of the system before pressure release to maintain the moisture content. Additives include natural and synthetic polymers, plasticizers and lubricants.^{136–139,159,160} The technology has been used to prepare pharmaceutical capsules and shaped objects, such as disposable cutlery, straws and pens.

A large portion of the disposable plastics market consists of products made from expanded polystyrene (EPS). A starch foamed extrudate prepared as loose fill from a hydroxypropylated, high-amylose (70%) corn starch provided very acceptable resilience and compressibility as compared to EPS loose fill. Chemically and physically modified high-amylose starches are more resistant to molecular degradation during high temperature–high shear processing than unmodified starch, and they also provide excellent foam cell structure and cushioning properties. The starch-based loose fill is stable over a range of humidity and temperature conditions and dissolves only on direct contact with water. In a soil environment, biodegradation is essentially complete.¹⁶¹ Resistance to humidity can be improved through the use of hydroxypropylated, high-amylose flours and hydrophobically modified high-amylose starches.^{162,163} A process for making biodegradable packing materials from non-high-amylose starch has been claimed.¹⁶⁴ Foamed starch compositions for packing, insulation, filler and cat litter can be prepared by extrusion at 150–250°F (65–120°C) and 30–70 bar.¹⁶⁵

Strengths of films made from a starch-poly(vinyl alcohol) blend containing glycerol and poly(ethylene-co-acrylic acid) have been examined.¹⁶⁶ High-amylose starches produced films with the most consistent properties. In a process for extruded blown film, blending of high-amylose starch with starches with more typical amylose contents and plasticizers or gelatinization aids improved properties.¹⁶⁷ Extruded

blends of starch and starch hydrolysis products (particularly maltodextrins, oxidized starches and pyrodextrins) are claimed to be useful molding materials.¹⁶⁸

Starch esters are useful in biodegradable applications; that application has been reviewed.^{169,170} In particular, high DS starch acetates provide thermoplasticity, hydrophobicity and compatibility with other additives. Starch acetates with a DS of >2.4 are not readily biodegradable.¹⁶⁹ Intermediate DS starch acetates are very biodegradable and have interesting properties. An aqueous slurry process has been developed for producing starch acetates or propionates with 0.5–1.8 DS.¹⁵⁰ The hydrophobicity provided by the ester groups in a product with 1.5 DS or about 30% by weight acetate ester groups makes it water insoluble. Partially depolymerized high-amylose (70%) corn starch acetate of intermediate DS formulated with plasticizer and wax to produce a hot melt adhesive for paper-to-paper bonding applications is water dispersible.¹⁷²

Other methods have been suggested for making high DS starch esters. Clear elastic films were produced from DS 2.5 starch esters made via reaction of starch in acetic anhydride with palmitic acid.¹⁷³ Starch acetates with >0.5 DS were prepared by reacting starch under nitrogen with equimolar amounts of acetic anhydride in N-methylpyrrolidone at the reflux temperature with 4-dimethylaminopyridine as a catalyst.¹⁷⁴ High DS (at least 2.8) starch acetates were prepared by reacting starch in excess acetic anhydride in the presence of sodium carbonate at the reflux temperature.¹⁷⁵ Uniform substitution was attained by swelling high-amylose corn starch in aqueous sodium hydroxide followed by precipitation and washing with methanol, then reacting the 'activated starch' with acetic anhydride.¹⁷⁶ Strength properties and water resistance are improved by extruding blends of starch acetate and low molecular weight esters (such as triethyl citrate).¹⁷⁷ Extruded blends of high DS starch esters and linear polyesters provide resistance to moisture-induced changes in molded articles.¹⁷⁸ A starch propionate (DS 1.5) plus other high DS (1.0–3.0) C₂–C₁₈ carboxylic acid esters can be used as paper surface sizing agents to provide increased tensile and burst strengths.¹⁷⁹

VI. Encapsulation/Controlled Release

Spherical porous aggregates of small starch granules (such as amaranth, rice and small wheat) have been prepared by spray drying a starch slurry containing a water-soluble gum as a bonding agent.¹⁸⁰ It was also suggested that calcium chloride could crosslink pectin or alginate used to coat the sphere to improve retention of the ingredient and sphere integrity.

Microporous starch granules are created by amylase treatment of native starch granules. This creates pinholes or pores leading from the surface to the granule interior. The sponge-like granules can absorb a variety of liquids. Chemical modification can be used to provide mechanical strength or alter receptivity. A coating can be applied to the starch granules to improve retention of the active or core material. Release is by mechanical compression, diffusion or degradation.¹⁸¹

Adherent starch particles were prepared by partially swelling pregelatinized starch in 30% 2-propanol and/or solutions of inorganic salts. A pest control agent was stirred into the gelled mass, which was dried, broken up and ground. The material

could be applied to plants after watering, allowing the active ingredient-containing particles to become sticky and adhere. An alternative method involved partially swelling pregelatinized starch in water containing sugary material, adding the active ingredient, and spraying the mixture directly onto plants.¹⁸² Swollen intact starch granules are prepared by controlled heating in a kneading extruder with 30–50% of a swelling agent, such as glycerol or triethanolamine, an emulsifier, such as a polyoxyethylene derivative of a sorbitan ester, and an oily material, such as a triglyceride. The emulsifier facilitates mixing of an active component into the swollen starch granules; the oil prevents the granules from fusing.¹⁸³ Encapsulation of vitamins, fragrance oil and concrete additives was accomplished in this way.

Core materials can be encapsulated by injecting them into freshly-cooked, temperature-stabilized, amylose-containing starch dispersions. Retrogradation of the starch on rapid cooling encloses the core material in a protective gel that can be dried and ground.^{184,185} The release rate of the core material decreases with increasing amylose content.¹⁸⁶ Incorporating an active agent into gelatinized native starch is conveniently accomplished by twin-screw extrusion.¹⁸⁷ Moisture content and particle size are important parameters. Use of highly crosslinked, swollen amylose matrices for controlled release of solid, orally delivered pharmaceutical products has also been described.¹⁸⁸ Extruded, biodegradable, controlled-release matrices for agricultural materials were prepared using high-amylose corn starch and synthetic polymers. Slight modification of the high-amylose starch with acetyl or hydroxypropyl groups improves processing of the hot melt. Crosslinking agents, fillers and plasticizers may also be used.¹⁸⁹ Stable starch–lipid composites are prepared by jet-cooking native starch slurries containing 20–50% of an oil, such as soybean oil.^{190,191} The jet-cooked starch–oil composites are stable and can be converted into dry powders by drum drying. The powders redisperse easily and can be used to improve the properties of starch–lipid formulations. Complete solubilization of the starch during cooking allows intimate contact with the oil, which is microencapsulated as small droplets (<10 μm) in the starch matrix.¹⁹² Suggested applications for the composites are to thicken, suspend, stabilize and replace fat. They may be useful as encapsulating agents for flavor oils, antioxidants, medicinal agents and agricultural materials for seed coating. A starch–oil composite was blended with a polyol polyester and the mixture was reacted with an isocyanate to produce a polyurethane foam.¹⁹³ Amylose complexation as a method for molecular encapsulation has been investigated.^{194,195} Chemical modification, e.g. by hydroxypropylation, improves the solubility of amylose complexes.^{196,197}

Starch octenylsuccinates are important commercial products for stabilizing a wide range of oil-in-water emulsions.^{198,199} Because they are good film formers, they provide an effective matrix for encapsulating volatile flavors and fragrances. They are approved for use as food ingredients. For spray drying applications, the starch is usually partially depolymerized to reduce the solution viscosity and allow a higher solids content to be used. Modified waxy starches are particularly effective in spray drying applications, due to enhanced solution stability. In a typical spray drying process, a starch octenylsuccinate is dissolved in water. Homogenization of the oil in the starch solution gives an effective emulsion with low particle size, which can now be spray dried to form hollow spheres. The oil is entrapped as droplets in the starch matrix

that forms the spheres. When the spray dried powders are added to water, the emulsion re-forms.

Improved stability towards oxidation of spray dried flavor oils was achieved by using a combination of a high-maltose syrup, maltodextrin and a high molecular weight, film-forming polysaccharide, such as starch octenylsuccinate or gum arabic.^{200,201} Emulsification performance of maltodextrins is improved by treatment with octenylsuccinic anhydride and aluminum sulfate.

A dual spray drying–extrusion process was used to produce glassy matrices for volatile or labile food components.²⁰² The spray dried, encapsulated food component was mixed with starch octenylsuccinate, a 10DE maltodextrin, corn syrup solids (24 DE) and maltose, and the blend was extruded to produce an amorphous melt. Another dual spray drying–extrusion process used starch octenylsuccinates to encapsulate a bleach catalyst for incorporation into a non-aqueous detergent formulation.²⁰² A process for producing readily dispersible, pregelatinized starch octenylsuccinates by extrusion has been described.²⁰⁴

VII. Physically Modified Starch

1. Granular Cold-Water-Swellable (CWS) and Cold-Water-Soluble Starch (Pregelatinized Granular Starch)

Cold-water-swellable (CWS) starch with the desirable characteristics of a starch paste prepared by cooking granular starch is required for instant foods. Traditional pregelatinized starches are prepared by roll drying, spray drying or extrusion (see Chapter 20). In spite of their wide use, these starch products are not able to match all the attributes provided by a starch paste prepared by cooking a slurry of granular starch. However, attributes such as dispersibility in hot or cold water, high viscosity and smooth texture are generally desirable for food products that require minimal home preparation. The general approach to overcome some of the shortcomings of traditional pregelatinized starch is to maintain starch granule integrity while providing cold water thickening. Two major classes of technology have been developed. One controls the swelling of starch granules in a mixture of water and an organic solvent. The other involves spray drying an aqueous starch slurry under carefully controlled conditions.

Pregelatinization of Starch in a Water-nonsolvent Solution

Aqueous alcohol: controlled granule swelling in aqueous alcohol was first reported in 1971,²⁰⁵ but was not put into practice until an improved procedure for preparing CWS was described.²⁰⁶ In this method, a slurry of granular starch in a solution of water in a water-miscible organic solvent, characteristically 70–80% alcohol, is heated to 157–177°C (315–350°F) for 2–5 minutes. Only slight degradation occurs. A slurry of such CWS common corn starch in a sugar or corn syrup sets to a sliceable gel without cooking or chilling and is useful in pie fillings, confectioneries, demoldable desserts and instant puddings. Blends of waxy and normal starches treated this way produce CWS products that have the properties of chemically modified starch

and disperse in hot or cold water without producing lumps, making them useful for instant and convenience foods.²⁰⁷

Alkaline alcohols: the aqueous alcohol process described above is not universally successful for all starches. Some products hydrate only in cold to warm sugar solutions without lumping, while others hydrate in cold water without lumping, but have reduced capacity to thicken. An improved process was described in 1991.²⁰⁸ In it, starch is treated with aqueous ethanol containing a strong base, such as sodium or potassium hydroxide, at 20–40°C for 20–40 minutes. The process provides a non-degraded, non-lumping product. The alcoholic alkaline process was used to produce a CWS hydroxypropylated granular starch useful for low calorie formulations such as instant desserts.²⁰⁹

Aqueous polyols: the aqueous alcohol process described above requires a pressure reactor which makes it undesirable from a manufacturing standpoint. In 1991, an atmospheric pressure process for production of granular cold-water-soluble starches was disclosed.²¹⁰ In it, a slurry of starch granules in water and a polyhydric alcohol, such as 1,2-propanediol, is heated at 145–155°C for ~15 minutes. Heating the slurry converts the starch crystalline structure to a V-type single helix crystalline arrangement or to an amorphous structure. The process is effective on cereal, tuber, root and legume starches, and on many of their crosslinked and substituted forms to yield cold-water-soluble starch granules having cold-water-solubilities of 70–95%.

Spray drying pregelatinization of starch: in 1981, a dual nozzle spray drying system to manufacture granular CWS starch was disclosed.²¹¹ A starch slurry is injected through an atomization aperture in a nozzle assembly to form a fine spray. Steam is injected through another aperture in the nozzle assembly into the atomized starch spray to gelatinize the starch, the entire operation taking place in an enclosed chamber. The time for passage of the material through the chamber, i.e. from the atomization aperture through the vent aperture, defines the cooking or gelatinization time. The gelatinized starch is recovered essentially as granules. The technology is broadly applied to both native and chemically-modified starches. For example, using this process, Schara and Katcher²¹² developed a pregelatinized, modified normal maize starch that is essentially flavor-free and which has a viscosity building capacity equivalent to spray dried and pregelatinized tapioca starch. In 1992, an improved process was reported.²¹³ In it, starch is uniformly and simultaneously atomized and cooked in an aqueous medium by means of a single atomization step in an apparatus comprising a two-fluid, internal mix, spray drying nozzle, coupled to a means for drying the cooked, atomized starch to produce a uniformly pregelatinized CWS starch with desirable textural, visual and organoleptic properties.

Other methods: alternative methods of producing lump-free CWS starch have been described. One employs heat–moisture treatment of a mixture of granular starch, a surfactant containing a fatty acid moiety and (optionally) a gum.²¹⁴ A process for making a corn starch product giving a uniform viscous dispersion when added to boiling water employs heating a mixture of starch, surfactant and water, followed by microwave radiation.²¹⁵ Compositions that gel at low solids concentrations were prepared by complexation of starches of moderate (20–30%) amylose content with emulsifiers.²¹⁶

2. Starch Granule Disruption by Mechanical Force

The size of fat globules or lipid micelles ($<3\ \mu\text{m}$) has triggered an examination of small starch granules as fat mimetics. Some starches such as amaranth, cow cockle, quinoa and rice, and fractions of other starches such as wheat, have small granules that have shown promise as fat replacers. However, their high production cost, because of the difficulty in isolating and purifying them, presently prohibits them from large-scale commercialization.

A process has been developed to produce a starch fat replacer by controlled acid-catalyzed hydrolysis of corn starch, followed by high pressure shearing of the starch slurry to a stable, cream-like gel consisting of aggregated starch crystallites.²¹⁷ Amorphous areas joining crystallites within granules are preferentially hydrolyzed, thus making the granule more fragile; shearing frees the crystallites. The molecular weight range of the hydrolyzate is generally between 3000 and 12000, preferably between 4500 and 6500. The preferred commercial starch is waxy maize starch. Typically, the product is supplied to users as hydrated granules, and a product with the consistency of a cream is prepared on-site by high pressure homogenization. A pregelatinized product has also been manufactured. This product has found wide applications as a fat substitute in products such as margarine, pourable and spoonable salad dressings, frostings and frozen novelties.^{218,219}

Jane et al.²²⁰ reported that mechanical attrition of the starch hydrolyzate in dry form also provides a small particle size and that the particles so produced also form a salve-like, fat-like paste when dispersed in water. Whistler²²¹ disclosed the preparation of starch-based fat substitutes from microporous starch prepared by amylase- or acid-catalyzed hydrolysis and then crosslinked before mechanical disintegration. The microporous starch can be modified by adsorption of a surface modifying agent or by reacting with an etherifying or esterifying reagent before the disintegration step.

VIII. Thermal Treatments

Effects produced by holding starch granules at various moisture contents and elevated temperatures have been the subject of extensive investigations.²²² Annealing or heat-moisture treatments alter the crystallinity of starch granules, especially those containing amylose. Typically, the starch gelatinization temperature is higher, the gelatinization endotherm is more defined and the energy value is increased (as determined by DSC) after the treatment. This scientific observation has been reduced to practice by Shi and Trzasko²²³ who generated a high-amylose starch with a higher dietary fiber content. Under preferred conditions, linear chains within granules realign themselves in a more orderly manner, thus making it more difficult for amylase attack. The resulting granular, high-amylose starch has a peak gelatinization temperature greater than 110°C . Starch with high dietary fiber content, i.e. starch that is more resistant to digestion, is more desirable than traditional cereal dietary fiber which has higher water adsorbitivity and gives a gritty texture. In addition to its functional benefits, resistant starch has been associated with physiological benefits, i.e. lowering

blood glucose and cholesterol concentrations and reducing the incidence of colon cancer.²²⁴

Non-chemically-modified starch that functions like chemically-modified starch is of great interest. Chemical modification is used to provide functionalities such as temperature, acid and shear tolerance during processing. Limited success has been achieved in simulating chemically crosslinked tapioca or potato starch by subjecting native amylose-containing starch to an annealing process.²²⁵ Several new, functional, native starches which have functional performance equivalent to traditional chemically-modified starches have been prepared. Their viscosity and process-tolerance profiles are similar to those of chemically crosslinked starches. In addition, the starches have a unique sensory property and a beneficial flavor release profile in various food systems. One such product is prepared by adjusting the pH to an alkaline value and then drying it.²²⁶ In another process, starch was treated with activated chlorine to produce a product that is temperature resistant like a conventionally crosslinked starch.²²⁷

IX. Enzyme-catalyzed Modifications

Currently, only hydrolases (amylases) are used to modify starch. The use of amylases to produce products derived from hydrolysis of starch is described in Chapters 7, 20, 21 and 22. Starch hydrolyzates with good adhesion property that can be applied at high solids to minimize the energy required to remove moisture after application are very desirable for coating food items with seasonings, flavors and colorants. This property can be achieved by treating starch with an amylase or amylases to a dextrose equivalency (DE) (see Chapter 21) of 2–40.²²⁸ Waxy maize is the preferred starch.

A low DE starch hydrolyzate with improved sweetness and browning capacity is prepared by treating starch with a combination of α - and β -amylase or α -amylase and glucoamylase (amyloglucosidase).²²⁹ A further improved process employs a heat-stable α -amylase to convert the starch, with recovery of the products at high temperature.²³⁰

A starch hydrolyzate with a peak average molecular weight of <10 000 that is capable of forming a gel was prepared by treating high-amylose starch with an α -amylase to a DE between 5 and 15.²³¹ The hydrolyzate is useful for preparing a foodstuff with reduced fat. Hydroxypropyl high-amylose starch hydrolyzate functions as a fat replacer.²³²

A hydroxypropylated starch hydrolyzate with a DP 2–6 (DE 20–45) functions as a bulking agent. When combined with a high-intensity sweetener, it is useful as a reduced calorie replacement for sucrose.²³³

A low-viscosity granular starch can be produced by contacting raw corn starch granules with an α -amylase in water.²³⁴ The preferred degree of hydrolysis is 0.1 to 1.0%.

Consumer healthy eating trends have generated the demand for functional fibers. Beta-glucan has been found to have desirable cholesterol-lowering benefits. Herwood²³⁵ disclosed a process for degrading cereal flour. New processing and/or physical modification techniques continue to ensure a constant stream of functional starch products into the marketplace. Conventional hybrid breeding and genetic

engineering offer the possibility of new base starches with varying properties that may show better performance in some applications than traditional native starches; chemical and/or physical modification of these new base starches should offer even more enhanced properties.

Concurrent with developments in starch technology, work is continuing with regulatory agencies to allow changes or additions to the list of approved starch derivatives. Enhanced characterization methods will aid this work and the development of new generations of starch products. A growing knowledge of the interactions of starch with other natural and synthetic polymers and various inorganic materials will allow the development of high performance, environmentally-friendly systems.

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