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Starch—Value Addition by Modification

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Starch is one of the most important but flexible food ingredients possessing value added attributes for innumerable industrial applications. Its various chemically modified derivatives offer a great scope of high technological value in both food and non-food industries. Modified starches are designed to overcome one or more of the shortcomings, such as loss of viscosity and thickening power upon cooking and storage, particularly at low pH, retrogradation characteristics, syneresis, etc., of native starches. Oxidation, esterification, hydroxyalkylation, dextrinization, and cross-linking are some of the modifications commonly employed to prepare starch derivatives. In a way, starch modification provides desirable functional attributes as well as offering economic alternative to other hydrocolloid ingredients, such as gums and mucilages, which are unreliable in quality and availability. Resistant starch, a highly retrograded starch fraction formed upon food processing, is another useful starch derivative. It exhibits the beneficial physiological effects of therapeutic and nutritional values akin to dietary fiber. There awaits considerable opportunity for future developments, especially for tailor-made starch derivatives with multiple modifications and with the desired functional and nutritional properties, although the problem of obtaining legislative approval for the use of novel starch derivatives in processed food formulations is still under debate. Nevertheless, it can be predicted that new ventures in starch modifications and their diverse applications will continue to be of great interest in applied research.

INTRODUCTION

Starch is one of the most important but flexible food ingredients possessing attributes for innumerable industrial applications.¹ It is widely distributed in the form of tiny granules as the major reserve carbohydrate in stems, roots, grains, and fruits of all forms of green leafed plants. Cereal grains, such as corn, wheat, sorghum, and tubers, and roots, such as potato, tapioca, arrowroot, etc., are some of the commercial sources of starch for industrial exploitation. Starch contributes significantly to the texture and sensory properties of processed foods.² It exhibits a wide range of functional properties, and it is probably the most commonly used hydrocolloid. One third of total starch produced is utilized for a variety of industrial applications that take advantage of its unique properties. Presently, the modern life is more and more dependent upon processed and convenience foods; it is almost impossible to live without them today.

Starch is a carbohydrate of high natural abundance next to cellulose³ and chitin.⁴ It is the most common constituent of human diet, where it accounts for the major share of energy

required for the sustenance of life. It is a macromolecular complex of at least two polymeric components, namely a linear and a highly branched α -D-glucan present in the ratio of $\sim 1:3$, respectively, both of which are essentially 1,4-linked, with the latter in addition having 1,4-linked branches attached to the main chain by 1,6-linkages. These two polymeric species are generally designated as amylose (Am) and amylopectin (Ap). Significant amounts of sparsely branched glucan chains (called anomalous Am or anomalous Ap) have also been identified in several grain starches,⁵ which together with other non-starch constituents account for poor digestibility characteristics, especially of some legume grains.⁶ The latter results in lowered and more prolonged post-prandial increase in blood glucose and may be of nutritional interest, for example, in the dietary management of diabetes.⁷

Starch granule differences amongst various plant species are accounted for, not only by the ratio of constituent molecules, but also by their location and interaction. Their interactions with other minor components, such as lipids and proteins, also influence the properties and the molecular architecture of the granules. A method using enzyme-gold cytochemical markers has been developed for the localization of amylose and amylopectin in starch granule.⁸ The shape of the granule appears to be modulated by the amylose content, especially in the appearance of concentric alternating layers.

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Starch, the adsorptive material in corn grits, is used as a natural desiccant in several industries.⁹ The porosity and other surface properties of starch can be suitably modified by a preliminary α -amylase treatment. The resulting material has better surface properties. Corn grit desiccants are known to be stable at both atmospheric and elevated temperatures and pressures. Corn grits are used as a desiccant in the production of alcohol to dry >750 million gallons of ethyl alcohol per year; this is an energy efficient process. Another application of corn grits is as a desiccant wheel dehumidification (to dry air) in large-scale outlets. The presence of more primary hydroxyl groups (due to side chain branching) in amylopectin allows it to have a greater adsorption capacity.¹⁰

STARCH—CHANGES DURING FOOD PROCESSING

As the major component of many foods, starch undergoes profound molecular, structural, and nutritional changes during processing of food raw materials. Often these changes are of technological utility, while others are detrimental to the quality of food. For example, upon long term grain storage at elevated temperature and in humid air amylases attack starch, especially the damaged starch, which results in increased water binding capacity of the flour.¹¹ The temperature of storage has a profound influence on the product making quality of stored potatoes. A sugar content of 0.2 to 6.8% formed upon storage affects the color and flavor of potato chips.¹² Excessive starch damage (during milling) is detrimental to bread quality. Partially gelatinized starch is capable of interacting with gluten, with the formation of a continuous phase of wheat dough with optimal rheological characteristics.¹³ For a good crumb texture such interactions are of great importance. The gelatinized starch along with gluten also provides a stabilizing network for retention of gas (formed during dough fermentation), thereby it prevents the collapse of the loaf volume during baking and cooling. An analogous property has been attributed to the functionally important mucilaginous polysaccharide of black gram in the preparation of leavened foods.¹⁴

In an excellent review on new industrial products of starch, Koch et al. have covered various facets of starch modification in relation to their varied industrial applications.¹⁵ As an auxiliary natural raw material of choice, starch has surpassed other similar biopolymers, such as cellulose in its versatility and usefulness. Many industrially important fermentation products are derived from starch carbohydrates or starch-based feed stocks.

Very often the viscosity of cooked native starch is so high it precludes its use in specific applications. For example, tuber starches on cooking give high peak viscosity, which upon continued cooking and cooling drops, contrary to cereal starches, which show moderate hot paste viscosity, but result in substantial increase in set back viscosity upon cooling; some starch dispersions are gummy and not palatable; amylose-rich starches form rigid, opaque gels on cooling (due to retrogradation), which on storage lose water (syneresis), whereas amylopectin-rich starches (waxy-type) form soft gels, etc.

The staling of bread¹⁶ is another quality attribute caused by starch retrogradation. The latter involves progressive association by extensive hydrogen bonding of glucan chains ultimately leading to a gel-like matrix. As a result, the bread crumb becomes firm, the crust loses its crispiness, and the flavor diminishes. Use of α -amylase during bread making results in the formation of low DP (2 to 7) malto-dextrins, which are responsible for the antistaling effect.¹⁷ During extrusion, starch undergoes profound gelatinization, which under pressure and shear may lead to degradation of starch.

Legume starches being rich in amylose may lead to extensive retrogradation as a result of close association between amylose chains and also between amylose and outer branches of amylopectin.¹⁸ Such an effect is prevented by esterification of starch. The introduction of as low as two such groups per 100 glucose residues is enough to hinder the alignment of linear chains and retard retrogradation. The resulting modified starch shows greater paste viscosity, paste clarity, and reduced syneresis.

The release of large amounts of dextrins by the action of amylases upon fermentation is followed by intense Maillard reactions that give a typical semi-sweet, roasted flavor and dark brown color.

STARCH—VALUE ADDITION BY MODIFICATION

To meet the demanding technological needs of today, the properties of starch are modified by a variety of modification methods. Starch modification is aimed at correcting one or some of the abovementioned shortcomings, which will enhance its versatility and satisfy consumer demand.¹⁹ Thus, the various chemically or otherwise modified starch derivatives offer significant value addition and give scope to develop a variety of fabricated food products having varied texture and mouthfeel.²⁰ These modifications are aimed at introducing desirable alterations in the starch structure so that its behavior is predictable and controllable. Therefore, the modified starch derivatives are the products of either glucosidic bond cleavage (acid modification to dextrins) or forming new functional groups (carbonyl group formation during oxidation), or substitution of free available hydroxyl groups (by etherification or esterification), or bridging of molecular chains by cross-linking reactions. Functional property modification is better exemplified by ionic hydrophilic substitution than by non-ionic hydrophobic substitution. In such functionalizations, the distribution of the introduced chemical substituents and of the remaining free hydroxyl groups within the anhydroglucose residue and along the polymer chain can exert a strong influence on the product properties. Some of the newly developed starch derivatives have been designed for non-food uses because of escalating costs for safety studies necessary to clear them for food use.

The various modifications employed are physical modification, non-destructive, and degradative chemical (and enzymatic) modifications. Hydrothermal treatments, such as extrusion cooking (processing and drying), radiation, sonication, and

pressure treatments, are the physical modification methods used; starch is (partially) gelatinized, resulting in decreased hydrogen bonding. Such starches are cold water dispersible and are generally used in cold water dispersible foods, such as ice creams, infant foods, dry baking premixes, etc. Annealing of starch is another hydrothermal modification, where the granular starch is heated in excess water at a temperature above the T_g but below GT . Although no total gelatinization of starch takes place, annealing brings in significant changes in some of its properties.²¹

Pre-gelatinization is the simplest of all starch modifications. It is effected by the cooking of aqueous starch slurry and subsequent drum drying. These starches are very useful in the preparation of ready-to-eat convenience foods, they give a palatable texture and help to hold other components in a uniform suspension. The market for such starches is steadily expanding. They are also useful as wall paper adhesives.

The different thermal processing treatments employed routinely in traditional cooking practices affect wheat starch properties to a considerable extent.²² The processing conditions vary considerably between the treatments, especially with regard to water content, pressure, temperature, and shear forces. Starch undergoes degradation during popping and extrusion cooking. The processed starch shows lower hot paste viscosity and higher water solubility. Gel permeation chromatography of such processed starch shows extensive macromolecular degradation.

Pyrodextrins are starch derivatives obtained by either dry heating or heating of the aqueous starch slurry with or without pH change. They are commercially very useful products for various applications. The extent of dextrinization reaction can be controlled to get well-defined, tailor-made products.²³ Depending upon the experimental conditions, different products, such as white dextrins, yellow dextrins, and British gums, are obtained. The three major reactions taking place during dextrinization are glycosidic bond cleavage (by hydrolysis), glycosidic bond formation (transglycosidation), and repolymerization. Increased branching was apparent upon dextrinization as evidenced by altered β -amylase digestion data, which indicates that the primary 6-OH groups are more reactive towards the formation of acetal linkages than secondary hydroxyl groups. Nevertheless, hydrolysis is the predominant reaction.

Photooxidation of starch in the presence of atmospheric oxygen gives rise to gluconic and glucuronic acids. The former further degrades to yield D-arabinose. The reaction is of free radical type involving glycosidic bond cleavage, as well as the cleavage of C-5 and C-1 bond of glucose residues.²⁴ The baking expansion characteristics of sour cassava starch have been attributed to photooxidation during sun drying, especially at 254 nm.²⁵ The extent of depolymerization was also dependent on the botanical origin of the starch source. For example, corn starch was refractory to such an oxidation. Staining with Schiff's reagent revealed aldehydic groups in photodegraded starch, and this reaction mechanism was akin to starch oxidation by periodate ions that results in the scission of C-2–C-3 bond, giving rise to dialdehyde groups. The HP-SEC profile showed random depolymerization products, essentially induced by free radicals.

The micronization (a physical damage induced by McCrone micronizing mill) of barley starch showed amylopectin of low molecular weight being preferentially solubilized in cold water.²⁶ Depending upon the conditions, more amylose was extracted into cold water.

Some studies have been made on the degradation of starch by polarized light.²⁷ Moonlight is assumed to be a source of polarized light.²⁷ Preliminary exposure to polarized light did not affect the crystalline structure of starch, although some changes in melting temperature and transition enthalpy were seen. Prolonging the exposure led to some degree of cross-linking, as shown by increased molecular weight. This has been attributed to activation of enzymes adhering to starch granule surface. Sensitivity of amylopectin to illumination exceeds that of amylose.

In the case of UV light induced starch degradation, the radiation is first absorbed by acetal chromophore at C-1 of glucose unit followed by further photoreaction.²⁸ Formation of peroxide ion at C-1 leads to gradual chain scission and reduced molecular weight, paste clarity/viscosity, and melting enthalpy. Prolonged irradiation leads to cross-linking with increase in molecular weight.

The surface derivatization of starch granules is another approach for bringing in desirable property changes. The complexing of amylose by lipid molecules influences both thermal and rheological properties of wheat starch, whereby the leaching of amylose molecules from the granules to the water is restricted.²⁹ Light microscopic studies show the presence of regions without birefringence, indicating lipid complexation. Such a surface modification with lipids would also affect starch gelatinization properties. For example, treatment with stearylchloride in CCl_4 and triethylamine (as catalyst) gives a starch derivative a fatty feel to the fingers.³⁰ It creates a carbohydrate-water network that can mimic the texture of fat. They are of use as fat replacers in frozen desserts.

Recently, a lot of concern has been shown by health conscious people on reducing the dietary calorie intake to avoid complications of obesity. Some of the starch derivatives are, indeed, being increasingly used as fat replacers or fat substitutes.³¹ They provide the mouth-feel of high fat emulsions in low fat or fat free products, lend a glossy, fat-like appearance, allow less fat pickup in some fried products, and are of use in the formulation of dietetic foods. They are either partially or totally undigested, thus contributing zero calories to the food on consumption. A lower rate of starch uptake also promotes a longer duration of satiety. The high water-holding capacity of some of the modified starches, which controls batter viscosity to aid in gas retention and starch and protein gelation, helps stimulating the moist mouth-feel of a high fat product. A number of fat mimetics, such as Maltrin, Oatrim, Amalean, Rice-Trim, Steller, etc., have been successfully commercialized in the west.³² Starch based fat replacers provide a slippery mouth feel when hydrated, and depending upon the modification type, the sensory perception varies. They work well in high moisture systems, such as salad dressings, meat emulsions, and some bakery products. They are not generally recommended for use in low moisture products.³³

In recent decades, a new fraction of starch called resistant starch (RS) has been discovered to have beneficial nutritional effects on humans. Information on the rate and/or extent of starch absorption, as influenced by starch properties, has led to an understanding of some of the nutritional characteristics of starch, such as the glycemic index (GI) and the RS content.³⁴ The latter depends on the choice of raw material and processing methods used. Low GI foods exhibit favorable effects on the control of diabetes and also on reducing risk factors for cardiovascular disease. Such foods, which are rich in RS, may be used as ingredient in the development of nutritionally balanced functional foods. RS is now recognized as an undigested starch fraction, formed upon food processing treatments and performing physiological functions akin to dietary fiber.³⁵ RS is nothing but a highly retrograded amylose fraction of starch that escapes digestion in the small intestine but is fermented later in the colon to short, chain fatty acids, especially butyrate.³⁶ Amylose is known to act as a restraint to swelling, but once swollen upon heating (gelatinization) and later allowed to cool gradually upon storage it leads to the development of crystallinity (retrogradation) caused by excessive hydrogen bonded entanglement and finally gives rise to RS. The incorporation of RS into the diet provides an opportunity to enhance the content of fermentable polysaccharide without altering the organoleptic characteristics of the food, but exerts a better physiological functioning. It has been shown that high amylose starches (amylomaize-type) increase proximal large bowel bacterial fermentation more than the normal starches.³⁷ Currently, RS is considered as man made dietary fiber of high physiological value. Chemically modified starch derivatives, for example, phosphorylated starches, which are also non-digestible, have been categorized as RS, similar to polydextrose or resistant oligosaccharides. The negatively charged phosphate groups, by acting as proton scavenger, preclude the hydrolytic action of amylases. The incorporation of RS in special food formulations is useful for diabetics and obese people. RS is a potential ingredient of low calorie foods.

The RS isolated from processed rice³⁸ and ragi³⁹ flour was shown to be linear α -1,4-D-glucan, probably derived from the retrograded amylose fraction. Prior defatting and autoclaving increased the RS content by 2 to 3 folds, whereas prior deproteinization did not show any major difference.⁴⁰ The RS fraction from several wheat-based products was similarly shown to be a low molecular weight α -D-glucan.⁴¹ Whereas from processed legume *dhal* flours, the recovery of RS was not high, in spite of the fact that legume starches are generally rich in amylose (~40%) component.⁴² As previously shown, both the molecular weight and degree of the branching of the constituent starch fractions (amylose and amylopectin) have a significant role in legume starch characteristics, especially the digestibility profiles.⁴³ Probably being rich in sparsely branched Am molecules or, in other words, low in truly linear Am chains, the net yield recovery of RS from legumes may be considerably low. The various additives and spices that are added during cooking of legume *dhals* in traditional food practices are shown to have some influence on RS formation and its recovery.⁴² Among

the starchy vegetables, green plantain showed a maximum RS content of 10.7 g% upon cooking.⁴⁴ It is shown that RS may also contribute to dietary energy, growth enhancement, and elevation in the fat deposition.⁴⁵

Non-destructive methods of starch modification refer to substitution reactions of free hydroxyl groups that bring about alterations in swelling and solubility properties, retrogradation characteristics, and functional attributes. Ionic, hydrophilic substitution is more effective than non-ionic, hydrophobic substitution. A variety of chemical modification methods are possible for starch, see Figure 1. The major advantages of such modifications are given in Table 1. The majority of such modified starches find extensive use in several non-food industries. For example, alkyl esters of starch are useful in textile finishing. Starch acetate, which are easily soluble in cold water even at high concentrations, are useful in paper and textile industries.⁴⁶ Similarly, starch xanthates and starch phosphates are effective binding agents in the paper industry. The carboxymethyl derivatives of starch are easily water soluble, even at low DS, and they form emulsions of high viscosity. In the food industry (see Table 2) they are useful as a water-imbibing agent during baking, as stabilizers in ice cream, as a glue in wall paper manufacture, and as improvers of printing dyes in the textile industry.¹⁹

High cationic properties have been observed for starch citrates.⁴⁷ The reaction is facilitated thermochemically by the dry heating (~120°C for 24 h) of citric acid to an anhydride, which reacts with starch to form an adduct, followed by further reaction to yield cross-linked starch citrate (see Figure 2). The reaction can be controlled to maximize reaction efficiency, minimize cross-linking, and maximize carboxyl content. They are used to remove toxic, heavy metal ions in water purification (industrial waste water) as biodegradable ion-exchange materials against the petrochemically derived ion-exchange resins. Recently, citrate starch has been used in food formulations as a source of RS.⁴⁸ Depending upon the degree of esterification, the RS content of derivatized starch can be altered.

Cationicity can also be introduced by reacting starch with trimethyl substituted quaternary amines.⁴⁹ The appearance of a sharp methyl group signal at 56 ppm in the ¹³C-NMR spectrum has allowed for quantitation of its DS. Substituents such as carboxylate, xanthate, acrylamide, and tertiary amine phosphate groups confer metal scavenging (chelating) property to starch.

Starch alkenyl succinate esters are prepared by a base catalyzed reaction of alkenyl succinic anhydride in aqueous medium.⁵⁰ The product (DS 0.02) exhibits surface active properties of use in stabilizing oil-in-water emulsions. The formation of strong films at the oil-water interface, unlike typical surfactants, gives resistance to emulsion from reagglomeration. They are useful in stabilizing flavor concentrates in beverages, salad dressing, flavor encapsulation, etc. They are also used as processing aids and in body powders/lotions. The octenyl succinate groups are found distributed in the interior amorphous domains of amylopectin and on the granule surface.

Hydroxyethyl starch, prepared by reaction with ethylene oxide, was of considerable biomedical interest as a blood plasma

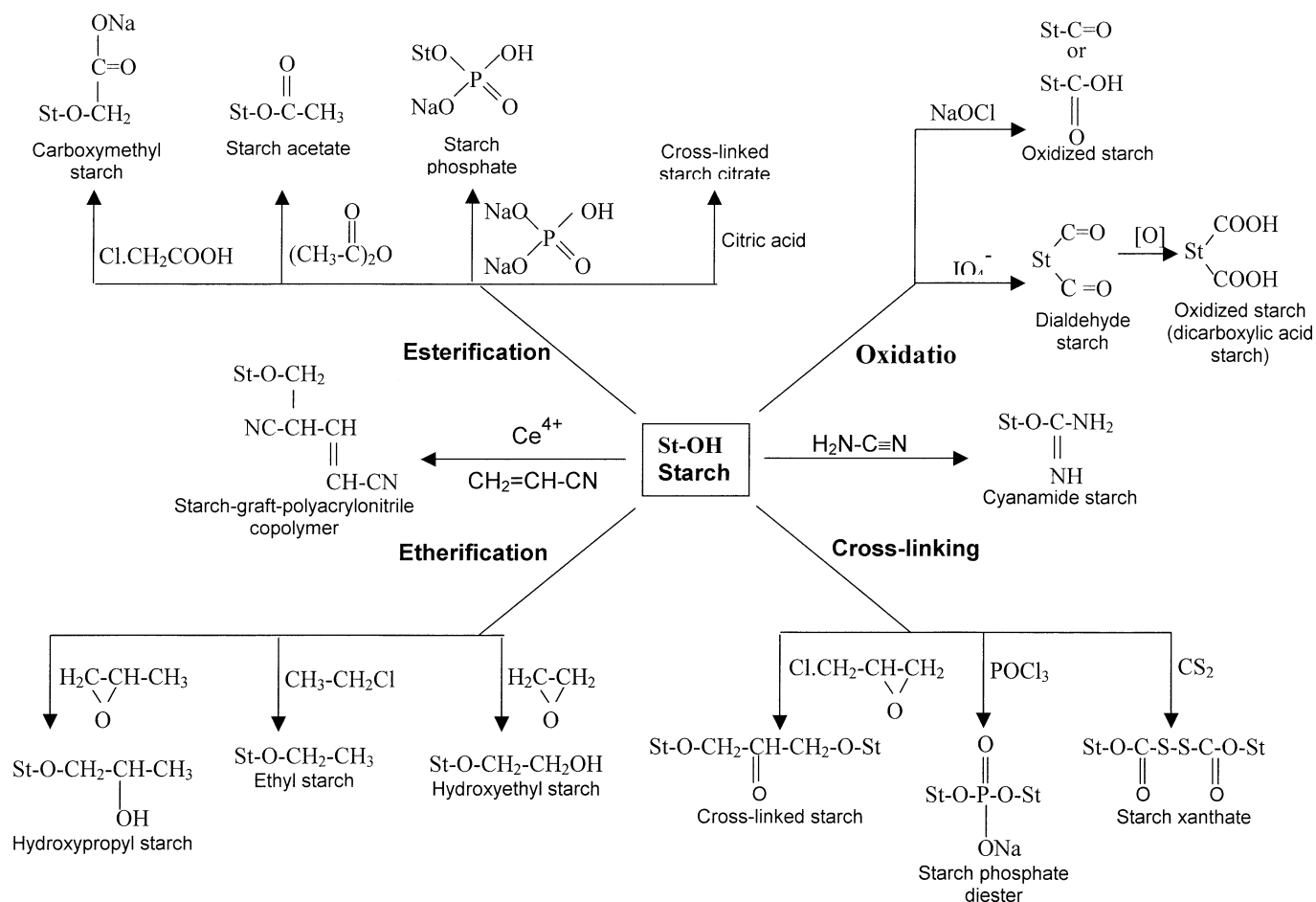


Figure 1 Starch modification reactions.

expander and also as a cryoprotective agent for erythrocytes.⁵¹ Modification by hydroxypropylation is especially interesting because of its toxicological safety and accommodative properties.⁵² Though all the three hydroxyl groups (at O-2, O-3 and O-6) are amenable for substitution, the derivatization mainly takes place at O-2. This is explainable on the basis of enhanced

reactivity of 2-OH under the strongly basic conditions used, due to the higher acidity of this hydroxyl group and also due to its proximity to the anomeric carbon (C-1). The substitution of O-6 takes place only at elevated temperatures, whereas the O-3 hydroxyl group is generally less reactive. The use of N₂ atmosphere during the reaction prevents oxidative degradation of the

Table 1 Characteristics of modified starches

Modification	Functional groups introduced	Properties/Applications
Pre-gelatinization	—	Cold water dispersibility— useful in instant convenience foods
Dextrinization	—	White/yellow dextrins—useful in baked goods
Anionic substitution	Carboxymethyl-phosphate-acetate-	Freeze-thaw stability—useful in frozen foods
Cationic substitution	Quaternary ammonium-	Lowered GT—useful as a pigment retention aid in paper, sizing-coating, textile wrapping
Hydroxypropylation	Hydroxypropyl-	Stabilizing agent—useful in processed foods, candies, low temperature stability
Cross-linking	Phosphate ester-Epichlorohydrin-	Granule stability, resistance to retrogradation, gelling—useful in soups, puddings, bakery products
Oxidation	Dialdehyde or dicarboxylic acid	Cross-link with amino/imino groups—useful in leather tanning, water resistance to adhesives
Partial acid or enzyme hydrolysis	Glycosidic bond cleavage	Increased retrogradation and set back—useful in confectionery, HFCS
Graft co-polymerization	Vinyl-acrylic-	Film making-biodegradability—useful in Biodegradable packaging films
Dual modification	—	Combination of properties—useful in bakery and frozen foods, salad dressings

Table 2 Starch hydrolysis products and their application

Product	Dextrose equivalent	Viscosity* cps	Sugars identified**				Application
			Glc	Fru	Mal	Dextrin	
Sugar syrups	42–63	75	25	30	5	2	Beverages, soft drinks, confectionery
Glucose syrups	98	110	98	—	2	—	Soft drinks, raw material for fermentation
Fructose syrups (HFCS)	—	520	5	90	—	—	Soft drinks, dairy products, canning industry
High maltose syrups	63	—	38	—	60	—	Candies, fermentation medium
Dextrimaltose (maltodextrins)	20	—	8	—	10	70	Stabilizers, pastes, glues, fillers

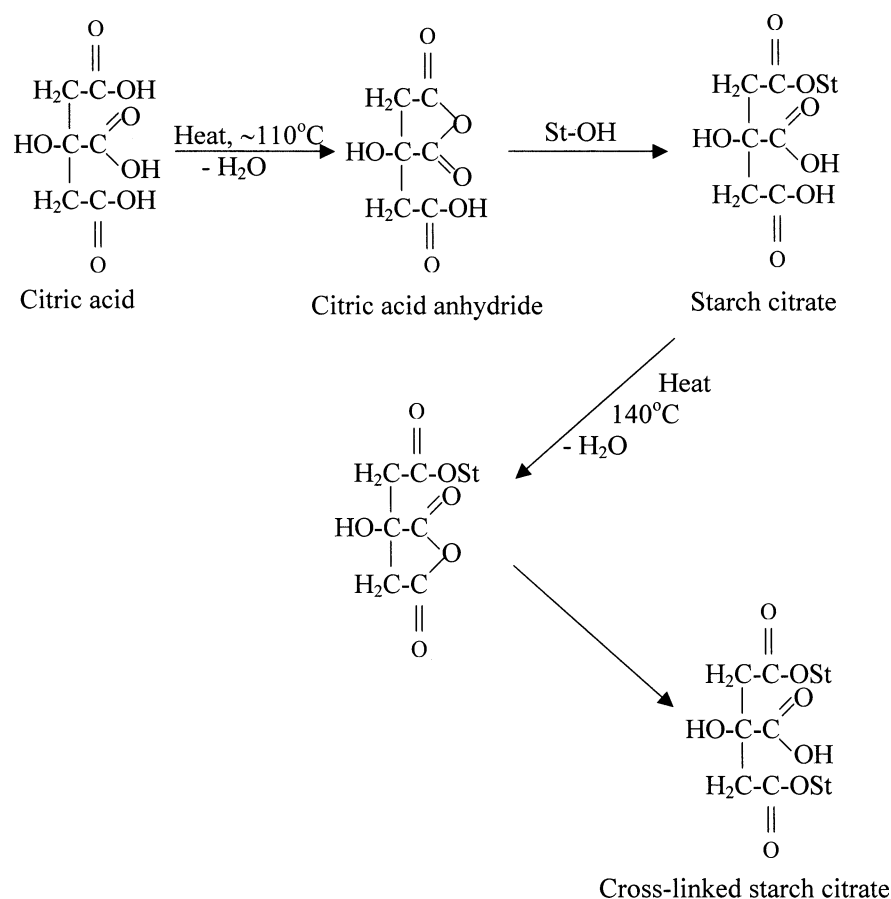
*Approximate value determined at 38°C.

**The percentage values given are approximate.

polymeric chain. Hydroxypropyl (HP) starches are designed to withstand vagaries of cooking, such as high temperatures, shear forces, and extremes of pH. HP starches offer pastes of increased clarity and freeze-thaw and cold storage stabilities. The substitution of HP groups takes place preferentially in the amorphous domains of amylopectin, with most of it at the C-2 hydroxyl group (67–78%), whereas at O-3 and O-6, it is 15–29% and 2–17%, respectively. Bulky HP groups prevent the alignment of starch chains (due to steric effects) and reduce starch retrogradation characteristics. HP starches have excellent film forming properties that are of use in biodegradable films. In general, starch ethers are more stable to cleavage by acids. By size exclusion

the chromatography of HP potato starch followed by enzymatic treatments, the location, and distribution of modifying groups have been delineated.⁵³ It has been shown that amylose was modified to a greater extent (molar substitution of 0.113) than amylopectin.

The carboxymethyl substitution of starch hydroxyl groups gives rise to derivatives that are cold water-soluble. To prevent starch gelatinization, the reaction has to be carried out in an organic medium.⁵⁴ Carboxymethyl starch, under the name sodium starch glycolate, is used in the pharmaceutical industry as a disintegrant and as a sizing and printing agent in the textile industry. Highly substituted derivatives are possible.

**Figure 2** Starch-citric acid reaction.

Starch phosphorylation is the earliest method of starch modification.⁵⁵ The reaction gives rise to either monostarch phosphate or distarch phosphate (cross-linked derivative), depending upon the reactants and subsequent reaction conditions. Monoesters, rather than diesters, are produced with a higher level of phosphate substitution on starch. The introduction of phosphate substitution on amylose or outer branches of amylopectin prevents linearity of molecular chains due to steric hindrance. Thus, a situation is achieved where individual chain segments can no longer approach each other closely enough to establish intermolecular or intramolecular association; they, therefore, lead to a better paste clarity. The phosphate diester starches have the phosphate esterified with two hydroxyl groups, very often from two neighboring starch molecules.⁵⁶ This leads to the formation of a covalent bridge or cross-linking. Phosphate cross-linked starches show resistance to high temperature, low pH, high shear, and leads to increased stability of the swollen starch granule. They improve viscosity and textural properties of the starch. As a thickener and stabilizer, starch phosphate diesters are superior to unmodified starches (see Table 3). They also provide resistance to gelling and retrogradation, and do not synerese on storage. Starch phosphates can substitute gum arabic (at ~0.5% level) in sugar syrups, ice cream mixes, salad dressing, and pudding.

Reagents, such as epichlorohydrin, phosphorus oxychloride, metaphosphate, citric, or adipic acids, react with starch forming intermolecular cross-linking of molecules.⁵⁷ Cross-linking can be considered as a means to “spot weld” the starch molecule at random locations, reinforcing hydrogen bonding and inhibiting granule swelling. In a way, by cross-linking, new branch points are introduced that will disorganize the crystalline domains of the polymer. Even a very low degree of cross-linking, for example, a cross-linking of one per 10,000 glucose residues, is sufficient to effect significant changes in starch properties and functionality. Cross-linked starches have peculiar hydration characteristics; they form highly viscous solutions in water and are used as high viscosity thickeners. Increased cross-linking results in an elevated GT and reduced swelling. In fact, very highly cross-linked starches are refractory for swelling, even when heated by autoclave sterilization, and they find use as dusting powders for surgical gloves. Cross-linking offers freeze-thaw stability and resists starch retrogradation. The latter is due to the

reinforcing effects of chemical covalent bonding, which is not as susceptible to rupture during cooking as are the hydrogen bonds.

Cross-linked starch is an ideal substitute for the expensive mung-bean starch in noodle making. It is also used as a polymeric base for controlled drug release. Since epichlorohydrin cross-linked starch is poorly water soluble and partly decomposes to glycerol, trimetaphosphate and phosphorus oxychloride are preferred cross-linking agents to get water soluble derivatives. Cross-linked starches are widely used in the food industry as thickeners, particularly where a high and stable viscosity is required. Cross-linking minimizes granule rupture, loss of viscosity, and formation of stringy paste during cooking.

Cross-linking of carboxymethyl starch with polyfunctional carboxylic acids, such as citric, malic, tartaric, etc., imparts considerable swelling capability, which can lead to stable hydrogels.⁵⁸ Their sturdiness depends upon the spacer length and availability of additional functional groups. Citric acid forms the most pronounced network structures.

CONTROLLED ACID/ENZYMATIC DEGRADATION

This is one of the earliest methods of starch modification, and the derived degradation products have a vast application potential. In its simplest methodology, the native granular starches are subject for treatment with acids, either at room temperature (for a period of several days) or at elevated temperature (for several hours). The extent of degradation is measured by the release of reducing sugar (called dextrose equivalent). Various starch hydrolysis products and their applications are given in Table 2. Our understanding of starch granule structure and its hydrolysis pattern are still far from complete. Many new processing operations of starch hydrolysis have been described that would be useful in food technological applications.⁵⁹ Care should be taken to avoid transglycosylation reaction (acid reversion) that occurs during acid hydrolysis. Products such as gentiobiose, maltose, cellobiose, trehalose, etc., have been identified during acid reversion step. The partial decomposition of glucose may lead to the formation of hydroxymethylfurfural, which is relatively a very reactive compound. This is subsequently broken down to formic and laevulinic acids.¹² Nageli dextrans, Lintner starch, etc., are some of the acid modified starch derivatives.²⁰ The degree of polymerization of amylopectin or acid modified corn starch drops from 1450 to 625, while that of amylose drops from 525 to 480.⁵⁹ A random attack at the branch point would create new linear chain segments that could appear as ‘apparent’ amylose and account for its observed increase.⁵⁹ Owing to problems encountered with acid hydrolysis, such as random attack, high yield of glucose, removal of acid later on, etc., the method is replaced by enzymatic hydrolysis.

The production of starch syrups (high fructose corn syrups, HFCS) by enzymatic method is amongst the most advanced food technologies (see Figure 3). It is probably the most successful enzyme technology of the food industry that is characterized by higher yields, wide range of products, higher product

Table 3 Some specific food applications of modified starch derivatives

Derivative	Applications
Esters	
Acetate ester	Cheese substitutes, improvement in noodle shelf life
Hexadecanoate ester	Thermally reversible gelation
Phosphate ester	Cheese substitutes, fruit jelly preparation, formation of foam with sodium caseinate
Ethers	
Carboxymethyl ether	Stabilizer of sour cream, ice cream, milk protein, slow release drugs and tablet molding
Hydroxyethyl ether	Cryoprotectant, blood substitute, fat emulsions
Hydroxypropyl ether	Dry mixes, puddings, salad dressings
Hydrogenated starch	Low calorie snack and candy

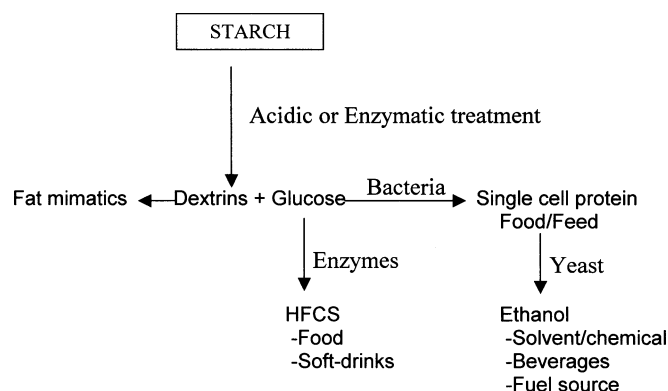


Figure 3 Value added products from starch (bio-) conversion.

quality and energy economy.⁶⁰ Methods have been standardized to use granular starches as such instead of gelatinized starch suspensions. Saccharification and liquification (thinning, decrease in viscosity) are the two major events taking place during starch amyolysis. The derived sugar syrups generally contain ~71% solids, of which fructose is 42%, glucose is 52%, and the rest are oligosaccharides. Syrups with higher fructose content (>90%) are also available, but they are expensive. These fructose-rich sugar syrups are highly valued in the food industry because of reduced calorie content and good tolerance by diabetics. They can be effectively used as fat mimetics and calorie reducers in flour-based dry mixes, baking systems, fillings, etc.

Some of the corn starch derived chemicals, namely D-glucose and its O-methyl glycoside, are convertible to polymerizable derivatives, such as allyl ethers, acrylates, and methacrylates, which can further be copolymerized to improve the properties.⁶¹ Some of the multifunctional monomers produced by them are extremely useful in thermoset applications, such as fibreglass insulation binders and plywood adhesive resins. Especially regarding the latter, methyl glucosides show remarkable formaldehyde scavenging properties in high formaldehyde resins. They are also useful as textile finishing resins. A host of highly useful non-food applications are envisaged for such chemicals derived from corn starch.

During the particleboard formation, the incorporation of starch hydrolyzates into urea-formaldehyde resins improves moisture stabilization of the resin and prevents oozing of formaldehyde in the hot press. Such resins also show improved burning behavior.⁶²

Recently, maltodextrins have been used as a biodegradable substitute for organic carrier liquids in ceramic molding.⁶³ Cross-linking helps preventing formation of cracks during thermal treatment. Glyoxal and glutaraldehyde are shown to be effective cross-linking agents for maltodextrins via acetalation-type reaction involving hemiacetal followed by acetal formation.

Cyclodextrins are another well known cyclic maltooligosaccharides having 6, 7, or 8 glucose residues linked by α 1,4-bonds and are called α -, β -, and γ -cyclodextrins, respectively.⁶⁴

They are produced by enzymatic conversion of liquefied starch by cyclodextringlucosyl transferases from *B. circulans* and *B. macerans*. Having a polar-hydrophilic exterior and an apolar-hydrophobic interior, cyclodextrins form inclusion complexes with hydrophobic molecules of suitable dimension and configuration. This property is made use of in the food, pharmaceutical and agrochemical industries.

OXIDATION

Oxidation is an useful modification method for bringing in changes in physicochemical properties of starch (see Table 1). Oxidative agents modify starch by forming new functional groups in the molecule. Oxidations with hypochlorite or more rarely with potassium permanganate are old methods but still used.⁶⁵ It involves conversion of primary hydroxyl group to carboxyl group. Because oxidation is an exothermic reaction, care must be taken to control the reaction temperature, lest an additional polymer chain degradation takes place.⁶⁶ The rate of oxidation is higher when carried out on gelatinized starch dispersion compared to granular suspensions. It is most rapid at neutral pH, and the reaction is controlled by lowering the pH and destroying the liberated chlorine. A low amount of carbonyl groups introduced during oxidation is beneficial for imparting stability to starch dispersions. A-type crystal structure of cereal starches, being more stable, is less reactive than B-type crystal structure of potato starch. The iodine binding power of oxidized potato starch decreases with increase in oxidation, probably due to Am being preferentially oxidized/degraded.

Periodate oxidation of starch leads to the session of C-2 and C-3 hydroxyl groups with the formation of dialdehyde or dicarboxylic acid derivative of starch. The reactive free aldehyde groups are capable of reacting with free amino- or imino groups to form rigid structures, a property made use of in hardening of paper and leather tanning. Acidic or neutral pH favors oxidation, and at high pH carboxyl groups are formed. The latter leads to increased hydrophilicity, provides steric bulk, interrupts linearity of the molecule, imparts anionic charge, and minimizes retrogradation. Dialdehyde starch that mixes with proteins (zein or soy protein) at high temperature and pressure cross-links by reacting with hydroxyls to form hemiacetals/acetals, or it can react with amino groups to form Schiff bases; it may also react with sulfhydryl groups. Bioplastics made out of such composites show increased tensile strength and percentage of elongation.⁶⁷ Darkening of color, due to decomposition during film molding by extrusion or thermopress method, can be eliminated by the incorporation of antioxidants. Dialdehyde starch is also used in medical applications as a chemical scavenger for urea and ammonia.⁶⁸ Dialdehyde or dicarboxyl starches could also be subjected to hydrolytic cleavage giving rise to D-erythrose and glyoxal or cleavage followed by hydrogenation yielding meso-erythritol and ethyleneglycol.⁶⁹ All these products have considerable industrial potential, although new approaches for such glycol cleavage are needed.

Periodate oxidized starch, called oxystarch, has been shown to be an excellent supporter for enzyme immobilization process.⁷⁰ A large amount of aldehyde groups, formed upon oxidation, reacts with amino groups of enzyme molecule forming Schiff's base and facilitates enzyme immobilization. Urease, immobilized on oxystarch, was shown to be superior to that of the original enzyme.

Nitric acid oxidation (>50% primary hydroxyl groups oxidized to carbonyls) gives a product highly useful in textile finishing, dietetic food, dip-in-water, and fat-proof covers.⁶⁶ Oxidized starches inhibit the tendency of starch to aggregate and lead to the formation of clear gels. They are readily soluble in water and are used in sugar confectionery and in foods where clear soft gels are required. A higher degree of oxidation leads to stable rigid films, a property of use in paper and textile industries, whereas low oxidized starches are useful in jelly production, colloidal stabilization of dairy products, etc. Very highly oxidized starches (random oxidation) show decreased water absorption due to the introduction of hydrophobic groups leading to hemiacetal formation and eventually cross-links.⁷¹ Oxidized starches have potentially several nutritive and non-nutritive applications of considerable value. The interaction of small amounts of dialdehyde starch with amino groups of wheat gluten improves dough properties and the quality of bread.

Air oxidation of potato starch over vanadium catalyst has been reported.⁷² The oxidation did not cause total destruction, instead, the process occurred on the surface and not in the granule interior. A clear erosion of the granule surface was observed, and the oxidized starch retained its granularity. Such oxidized starch products have applications as ink thickeners, coatings, and detergent builders. The oxidized starch gives more viscous gels than unprocessed starch. Oxidized starches are widely used in papermaking, especially to close the pores of paper, to lay fuzz on the surface and to increase the tensile fold and bursting strength. Excellent divalent metal ion (Cu^{2+} , Zn^{2+} , Pb^{2+} , and Cd^{2+}) binding of succinylated and oxidized starches has been described.⁷³

BIODEGRADABLE MATERIALS

Growing interest has been shown in the incorporation of starch into plastics to make them biodegradable. Such a biopolymer replacement, though only partial, is attractive to conserve dwindling petroleum resources. Their potential benefits are environmental and cost related. Although the biopolymer (starch) has poor mechanical properties, blending gives bio-fragmentable materials with improved mechanical properties.⁷⁴ The incorporation of prooxidants and/or photosensitive agents will promote better degradation, especially synthetic plastics, which are petroleum based. The use of starch as a thermoplastic material is of recent origin. Compared to starch films, low dextrose equivalent dextrans and corn syrup were more resistant to water vapor transport.⁷⁵ Films of starch hydrolysates have shown some resistance to oxygen transmission. The dipping of fresh sliced apples

in a starch hydrolysate (40% solution) having a dextrose equivalent value of 15 prior to dehydration prevented browning of the tissue, probably by retarding the entrance of oxygen.⁷⁶ The commercial exploitation of such edible films and coatings for sustainability of product freshness and also possibly microbial stability is yet to be fully realized. Such biodegradable polymer composites can be prepared by either extrusion cooking (extrusion-blow film technology) of the well mixed ingredients or by graft copolymerization.⁷⁷ In the latter, the natural and the synthetic components are held together by covalent bonding, rather than existing merely as a physical mixture, as in the former. Graft co-polymerization is essentially a free radical reaction, where starch upon treatment with ceric ammonium nitrate yields free radical sites on the glucan backbone which act as microinitiators in the presence of synthetic monomers to yield polymer grafts of high molecular weight.⁷⁸ Using potassium persulphate as the radical initiator, a series of starch-graft-copolymers of vinyl monomers, such as acrylamide, acrylonitrile, acrylic acid, and methacrylic acid, have been prepared, and their properties studied.⁷⁹ Their main use is for cotton sizing. Cationic starch-graft-copolymers, prepared by graft co-polymerization of starch with amino compounds, are highly useful as flocculating agents in water purification systems and as retention aids in the manufacture of mineral-filled paper.^{80,81} They are also useful as effective clay or shale hydration inhibitors in oil field treatment. Such derivatives enlarge the industrial uses of starch. A lot of work has gone into the preparation of starch-graft-polyacrylonitrile⁸² and starch-graft-polymethacrylate⁸³ copolymers and their mechanical properties. These can be extruded for use as expanded packaging material or foamed protective packaging material that can replace traditional expanded 'polystyrene peanuts'.⁸⁴ Such starch-based loose fills contain a variety of biodegradable polymers and additives that will improve resiliency and compressibility and aid in processing. Low shear conditions during extrusion produce loose fills that are both brittle and heavy, regardless of the type of starch used.

The process of the disordering of amylose and amylopectin chains through the melting of crystallites taking place during heating of starch with limited amounts of water is called 'destructured starch'.⁸⁵ The latter is useful in the development of extrusion-blown films from starch and poly(ethylene co-acrylic acid) graft copolymers. As much as 50% of the weight of starch can be incorporated into such composites, yet still retain acceptable properties. Bio-Pac packages consist of potato starch, maize starch, wheat starch, and other similar raw materials that in the presence of water are finally baked and conditioned.

To overcome the formation of homopolymerization of synthetic monomers during grafting to a considerable extent, intermediate formation of diazonium compounds from starch esters, such as anthranilates, has been developed, which creates primary free radicals directly on the starch molecule and favors enhanced graft copolymerization.⁸⁶ By variation in their ratio and mix-up, products are prepared that absorb more than 1000 g water. Such super absorbents are very useful in hygienic and sanitary product manufacture. Polymer grafted sago starch has

been further modified by reacting with hydroxylamine to obtain derivatives having the property of high water absorption (192 g water/g material at 31% starch in the absorbent).⁸⁷ Such products are useful in feminine napkins, disposable diapers, water blocking tapes, medicine and agriculture, where water absorbency or water retention is important.

The use of plasticizers in such systems modifies their mechanical properties by decreasing intermolecular attractions between adjacent polymeric chains, thus increasing film flexibility and changing barrier properties.⁸⁴ Water is considered to be a universal plasticizing agent of value in several applications.⁸⁸ It is shown from X-ray diffraction results that the plasticizer decreases the activation energy for the formation of the most stable crystalline structure of the polymer.⁸⁹ Due to incompatibility, the use of excessive concentrations of plasticizer leads to phase separation and its exclusion, which appears like a white residue on the surface of the film. This is referred to as the 'blooming' effect. By extrusion of native starch with glycerol (used as plasticizer), thermoplastic starch has been obtained by the formation of inter-molecular double helical structures of amylose and amylopectin. The formation of physical cross-links further stiffens starch crystallinity and strengthens the polymeric network.

High amylose starches are shown to give better films than normal starches. Freestanding films made from high methoxy pectin, and high amylose starches are shown to have good mechanical and barrier properties of use in a few specific packaging applications.⁹⁰ High molecular weight with a higher degree of esterification of pectin provides the best quality of films. The use of glycerol, which is thermally stable up to 180°C, as a plasticizer is necessary to make the film flexible and non-brittle. The use of starch in such films has the advantages of reducing the material cost and improving the surface properties. Films made out of only starch and glycerine are too brittle and not conducive for handling. By combination of different polymers in different proportions, a range of bio-films with varying properties could be prepared.

Considerable research and development efforts have been made on BIOPAC packages consisting of materials rich in starch and a few other additives.⁹¹ Together with water, these ingredients are baked and conditioned, which facilitates their total degradation within a matter of weeks. BIOPAC trays are light porous materials having a density <0.25, therefore, they have good heat insulating and shock absorbing properties. They are made in different forms, such as trays, cups, boxes, cartons, etc., and they are generally used for storing dry products with low humidity. This packaging material makes good use of agricultural over-production, being easily biodegradable, it contributes to a dramatic reduction in garbage volume. Starch-based porous shaped foam articles are of use as packaging materials in fast food operations and also in agriculture.⁹² For the latter, the use of biodegradable plastic films are becoming increasingly important, because their use for agricultural mulching controls weeds, conserves soil moisture and heat for early cropping, and reduces nutrient leaching. A starch-graft-poly (methylacrylate) copolymer has been prepared having grafted side chains with

molecular weight <500,000. The extruded film had excellent tensile strength and elongation. Preliminary studies indicated substantial biodegradation, especially of the starch portion of the copolymer incubated with *Aspergillus niger*.⁹³

As biodegradable composites, a combination of starch with polyolefins (1:1) gives a product having anti-blocking behavior, good printability, and improved water vapor permeability for films.⁹⁴ Modified starches are incorporated in liquid systems, such as PVC plastics or styrene-butadiene copolymer blends, for carpet backing; these give a homogeneous surface of the back foam with improved drying properties. To avoid incompatibility between starch and polyethylene, ethylene is directly polymerized in the presence of starch, a process that is facilitated by alumoxan and transition metal complexes.⁹⁵ Such a system is reported to give very high polyethylene-starch composites containing up to 95% of starch. Microscopic observations have shown starch granules that are completely covered with crystalline polyethylene blocks.

Hydroxylapatite-reinforced starch composites are considered as new materials for biomedical application. Kaolin, a naturally occurring hydrated aluminosilicate, is used in compositions of rubber, plastics, and paints. Composites of thermoplastic starch and kaolin have shown on scanning electron microscopy a very good dispersion of the latter, which also helps in reducing the water uptake of the composites.⁹⁶

The biodegradation of such polymer-based composites can take place by various means. After disposal in landfills (compost), they may be degraded by sunlight, catalysts (photodegradation), water, oxygen (chemodegradation), microorganisms, enzymes of the soil/environment (biodegradation), and by wind/atmosphere (mechanical degradation), or a combination of all these into environmentally safe, harmless products. Excellent susceptibility to fungal growth has been observed in a moist environment for starch-graft-co-polymers. The use of such films for agricultural mulching has become increasingly more important. Such usage controls weeds, conserves soil moisture and heat for early cropping, and reduces nutrient leaching. As the starch portion is utilized by the organism, the available surface area of the degraded co-polymer is increased, which in turn enhances further microbial and oxidative degradations.

The biodegradation of starch-graft-polyacrylonitrile has been studied both by *in vitro* and *in vivo* systems.⁹⁷ The initial depolymerization of polyacrylonitrile chains by *Bacillus cereus* occurred by the extracellular peroxidase, whose activity was maximum after 3 h. Later, the intracellular nitrile hydratase and amidase cleaved the released free acrylonitrile residues into acrylamide and acrylic acid, respectively, as determined by the recently developed reverse phase HPLC method.⁹⁸ The starch moiety was degraded to low molecular weight dextrin-type products by the extracellular α -amylase, whose activity was maximal after ~8 h of growth. For the *in vitro* degradation, different amylolytic enzymes were used, and the maltooligosaccharide profiles were analyzed by HPLC. Low molecular weight polyacrylonitrile chains were identified in the amylolyzates treated with *B. cereus* cells.⁹⁹

The biodegradability of food packaging material might envisage a wide range of attractive business opportunities based on consumer demand for safe non-synthetic packaging materials.¹⁰⁰ Under the trade name AMYPOL, biodegradable starch-based resins have been prepared as a 'peanut' shaped loose-fill for various packaging applications. This material contains a low DS propoxylated high amylose starch, and it is used as a successful replacement for non-biodegradable expanded polystyrene loose-fill packaging.⁵⁴

Several formulations of polyurethane foams with corn starch and/or corn flour have been prepared for use as absorbent materials in cleaning pads, disposable diapers, sanitary napkins, sponges, and horticultural products.¹⁰¹ Some of the foams exhibit excellent thermal stability and thermal conductivity properties of value for a variety of speciality applications. However, in some specific applications, the biodegradability of such starch-based polymer composites is of great disadvantage. For example, the incorporation of starch as its xanthide or as xanthate salt into natural rubber (by co-precipitation method) offers a superior vulcanizing effect that is of use in general purpose goods, such as shoe soles and passenger tire tread.¹⁰² These have to encounter the wrath of heat, stress/strain, moisture, and soil in their outdoor service conditions. Reducing the biodegradability in such applications is of economic gain. This has been achieved by cyanoethylation of starch xanthide. As a substituent, cyanoethyl groups offer much greater resistance to biodegradation than xanthide groups. Here, the biodegradation tests were carried out by soil burial method under ambient conditions for extended duration (45 d) and the results showed no discoloration (turning to deep brown or black) or roughening of the surface. A moderately higher degree of cyanoethylation (DS = 0.8) and a somewhat low level of xanthation (DS = .1) on starch-filler offered a very high resistance to biodegradation of starch-vulcanizate rubber without sacrificing its vital tensile properties.

BIOTECHNOLOGICAL APPLICATIONS

Starch and its partially hydrolyzed products (dextrins, maltose, and glucose) are an excellent fermentation base for the bulk production of a wide variety of biotechnological products, such as organic acids, antibiotics, vitamins, hormones, etc. As a sole carbon source providing energy for maintaining biological functions, starch derived carbohydrates are of very high commercial value (see Figure 3). The oxidation of glucose by bacterial fermentation using *Aspergillus niger* or *Acetobacter suboxidans* yields gluconic acid (>97% yield).¹⁰³ Sodium gluconate is the most useful salt, used as a chelating agent to produce deltagluconolactone, which is useful as an acidulant in food processing.¹⁰⁴ Microbial fermentation of glucose using *Xanthomonas campestris* yields xanthan gum, a very useful commercial hydrocolloid.¹⁰⁵ Osmophilic yeast *Moniliella tomentosa* utilizes glucose to convert into erythritol, which is an interesting, useful C-4 polyol with a functionality of 2-primary and 2-secondary hydroxyl groups.¹⁰⁶ It is used in the manufacture of polyurethanes, alkyl resins, etc.

Starch derived glucose can be fermented to produce lactic acid, which can either be polymerized or graft-co-polymerized to poly(lactic acid) polymer or composites having use as biodegradable films or bioplastics.¹⁰⁷ Potato starch waste is used as a feed stock in such fermentative reactions. High molecular weight copolymers, which are spliced through using suitable coupling agents, have excellent mechanical properties. The dehydrated dimer, the lactide, upon ring opening polymerization, gives high molecular weight polylactide polymers that are of use in a number of biomedical applications, such as resorbable sutures, prosthetic devices, drug delivery systems, etc.¹⁰⁸ Several polyhydroxyalkanoates are prepared using a variety of starch based feed-stocks.

CONCLUSIONS

In conclusion, it seems obvious that the technological potential and industrial utility of starch gets multiplied by several folds by suitable modification, as exemplified in this article and other contemporary literature. Although legislative approval for the use of novel starch derivatives in processed food formulations is still under debate, many tailor-made starch derivatives with multiple modifications are being prepared and characterized. In the area of thermoplastic bio-packaging, the usefulness of starch is much more significant and rewarding. Synthetic polymers are gradually being replaced by biodegradable polymers. It may be predicted that eventually biodegradable packaging will find larger and more receptive markets in future. Surely, tomorrow's packaging needs will be dictated by such biodegradable materials/composites. By the specific functionalization of starch, new products are continuously being developed that find increasing use in a wide variety of industrial applications, leading to a significant value addition. With the explosion of interests and the availability of a very wide variety of such bio-packaging materials in recent years, it is only natural that there can be no boundaries—only possibilities.

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