# Carbohydrates

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Carbohydrates comprise more than 90% of the dry matter of plants. They are abundant, widely available, and inexpensive. They are common components of foods, both as natural components and as added ingredients. Their use is large in terms of both the quantities consumed and the variety of products in which they are found. They have many different molecular structures, sizes, and shapes and exhibit a variety of chemical and physical properties. They are amenable to both chemical and biochemical modification, and both modifications are employed commercially in improving their properties and extending their use. They are also safe (nontoxic).

Starch, lactose, and sucrose are digestible by humans, and they, along with D-glucose and D-fructose, and human energy sources, providing 70–80% of the calories in the human diet worldwide. In the United States, they supply less than that percentage, in fact only about 50%, of the human caloric intake. Health organizations recommend that the percentage of the total calories the average American consumes in the form of fat (about 37%) be reduced to no more than 30% and that the difference be made up with carbohydrate, especially starch.

The term carbohydrate suggests a general elemental composition, namely C\(_x\)(H\(_2\)O)\(_y\), which signifies molecules containing carbon atoms along with hydrogen and oxygen atoms in the same ratio as they occur in water. However, the great majority of natural carbohydrate compounds produced by living organisms do not have this simple empirical formula. Rather, most of the natural carbohydrate is in the form of oligomers (oligosaccharides) or polymers (polysaccharides) of simple and modified sugars. Lower molecular weight carbohydrates are often obtained by depolymerization of the natural polymers. This chapter begins with a presentation of the simple sugars and builds from there to larger and more complex structures.

4.1 Monosaccharides [8,27]

Carbohydrates contain chiral carbon atoms. A chiral carbon atom is one that can exist in two different spatial arrangements (configurations). Chiral carbon atoms are those that have four different groups attached to them. The two different arrangements of the four groups in space (configurations) are nonsuperimposable mirror images of each other. In other words, one is the *Carbohydrates that cannot be broken down to lower molecular weight carbohydrates by hydrolysis are monosaccharides, a term that indicates that they are the monomeric building units of the oligo- and polysaccharides. Monosaccharides are commonly referred to simply as sugars. However, as will be explained later, table sugar (sucrose) is not a monosaccharide.*
reflection of the other that we would see in a mirror, with everything that is on the right in one configuration on the left in the other and vice versa (Fig. 1).

D-Glucose, the most abundant carbohydrate and the most abundant organic compound (if all its combined forms are considered), belongs to the class of carbohydrates called monosaccharides. Monosaccharides are carbohydrate molecules that cannot be broken down to simpler carbohydrate molecules by hydrolysis, so they are sometimes referred to as simple sugars. They can be joined together to form larger structures, namely, oligosaccharides and polysaccharides (see Secs. 4.2 and 4.3), that can be converted into monosaccharides by hydrolysis.

D-Glucose is both a polyalcohol and an aldehyde. It is classified as an aldose, a designation for sugars containing an aldehyde group (Table 1). The ending -ose signifies a sugar; and signifies an aldehyde group. When D-glucose is written in an open or vertical, straight-chain fashion, known as an acyclic structure to organic chemists, with the aldehyde group (position 1) at the top and the primary hydroxyl group (position 6) at the bottom, it is seen that all secondary hydroxyl groups are on carbon atoms having four different substituents attached to them.

<table>
<thead>
<tr>
<th>Number of carbon atoms</th>
<th>Aldehyde</th>
<th>Ketone</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Triose</td>
<td>Triulose</td>
</tr>
<tr>
<td>4</td>
<td>Tetrose</td>
<td>Tetrulose</td>
</tr>
<tr>
<td>5</td>
<td>Pentose</td>
<td>Pentulose</td>
</tr>
<tr>
<td>6</td>
<td>Hexose</td>
<td>Hexulose</td>
</tr>
<tr>
<td>7</td>
<td>Heptose</td>
<td>Heptulose</td>
</tr>
<tr>
<td>8</td>
<td>Octose</td>
<td>Octulose</td>
</tr>
<tr>
<td>9</td>
<td>Nonose</td>
<td>Nonulose</td>
</tr>
</tbody>
</table>
These carbon atoms are therefore chiral. Glucose has four chiral carbon atoms: C-2, C-3, C-4, and C-5. Naturally occurring glucose is designated as the D form, specifically D-glucose. It has a molecular mirror image, termed the L form, specifically L-glucose. Since each chiral carbon atom has a mirror image, there are $2^n$ arrangements for these atoms. Therefore, in a six-carbon aldose, there are $2^4$ or 16 different arrangements of the carbon atoms containing secondary hydroxyl groups, allowing formation of 16 different six-carbon sugars with an aldehyde end. Eight of these belong to the D-series (see Fig. 3); eight are their mirror images and belong to the L-series. All sugars that have the hydroxyl group on the highest numbered chiral carbon atom (C-5 in this case) positioned on the right-hand side are arbitrarily called D-sugars, and all with a left-hand positioned hydroxyl group on the highest numbered chiral carbon atom are designed L-sugars. Two structures of D-glucose in its open-chain, acyclic form (called the Fischer projection) with the carbon atoms numbered in the conventional manner are given in Figure 2. In this convention, each horizontal bond projects outward from the plane of the page and each vertical bond projects into or below the plane of the page. It is customary to omit the horizontal lines for covalent chemical bonds to the hydrogen atoms and hydroxyl groups as in the structure on the right. Because the lowermost carbon atom is nonchiral, it is meaningless to designate the relative positions of the atoms and groups attached to it. Thus, it is usually written as -CH$_2$OH.

D-Glucose and all other sugars containing six carbon atoms are called hexoses, the most common group of aldoses. The categorical names are often combined, with a six-carbon-atom aldehyde sugar being termed an aldohexose.

There are two aldoses containing three carbon atoms. They are D-glycerose (D-glyceraldehyde) and L-glycerose (L-glyceraldehyde), each possessing only one chiral carbon atom. Aldoses with four carbon atoms, the tetroses, have two chiral carbon atoms; aldoses with five carbon atoms, the pentoses, have three chiral carbon atoms and comprise the second most common group of aldoses. Extending the series above six carbon atoms gives heptoses, octoses, and nonoses, which is the practical limit of naturally occurring sugars. Development of the eight D-hexoses from D-glycerose is shown in Figure 3. In this figure, the circle represents the aldehyde group; the horizontal lines designate the location of each hydroxyl group on its chiral carbon atom, and at the bottoms of the vertical lines are the terminal, nonchiral primary hydroxyl groups. This

![Figure 2](image)

**Figure 2**
D-Glucose (open-chain or acyclic structure).
shorthand way of indicating monosaccharide structures is called the Rosanoff method. Sugars whose names are in italics in Figure 3 are commonly found in plants, almost exclusively in combined forms. They therefore are present in our diets in combined froms, D-Glucose is the only free aldose usually present in natural foods, and then only in small amounts.

L-Sugars are less numerous and less abundant in nature than are the D forms but nevertheless have important biochemical roles. Two L-sugars found in foods are L-arabinose and L-galactose, both of which occur as units in carbohydrate polymers (polysaccharides).

In the other type of monosaccharide, the carbonyl function is a ketone group. These sugars are termed ketoses. (Ket- signifies the ketone group.) The suffix designating a ketose in systematic carbohydrate nomenclature is -ulose (Table 1). D-Fructose (Fig. 4) is the prime example of this sugar group. It is one of the two monosaccharide units of the disaccharide sucrose (see Sec. 4.2.3) and makes up about 55% of high-fructose corn syrup and about 40% of honey. D-Fructose has only three chiral carbon atoms, C-3, C-4, and C-5. Thus, there are only 2^3 or 8 D-ketohexoses. D-Fructose is the principal commercial ketose and the only one found free in natural foods, but, like D-glucose, only in small amounts.

4.1.1 Monosaccharide Isomerization

Simple aldoses and ketoses containing the same number of carbon atoms are isomers of each other; that is, a hexose and a hexulose both have the empirical formula \( \text{C}_6\text{H}_{12}\text{O}_6 \) and can
be interconverted by isomerization. Isomerization of monosaccharides involves both the carbonyl group and the adjacent hydroxyl group. By this reaction, an aldose is converted into another aldose (with opposite configuration of C-2) and the corresponding ketose, and a ketose is converted into the corresponding two aldoses. Therefore, by isomerization, D-glucose, D-mannose, and D-fructose can be interconverted (Fig. 5). Isomerization can be catalyzed by either a base or an enzyme.

4.1.2 Monosaccharide Ring Forms

Carbonyl groups of aldehydes are reactive and easily undergo nucleophilic attach by the oxygen atom of a hydroxyl group to produce a hemiacetal. The hydroxyl group of a hemiacetal can react further (by condensation) with a hydroxyl group of an alcohol to produce an acetal (Fig. 6). The carbonyl group of a ketone reacts similarly.

Hemiacetal formation can occur within the same aldose or ketose sugar molecule wherein the carbonyl function reacts with one of its own properly positioned hydroxyl groups, as illustrated in Figure 7 with D-glucose laid coiled on its side. The resulting six-membered sugar ring is called a pyranose ring. Notice that for the oxygen atom of the hydroxyl group at C-5 to react to form the ring, C-5 must rotate to bring its oxygen atom upward. This rotation brings the hydroxymethyl group (C-6) to a position above the ring. The representation of the D-glucopyranose ring used in Figure 7 is termed a Haworth projection.

Sugars occur less frequently in five-membered (furanose) rings (Fig. 8).
To avoid clutter in writing the ring structures, common conventions are adopted wherein ring carbon atoms are indicated by angles in the ring and hydrogen atoms attached to carbon atoms are eliminated altogether. A mixture of chiral forms is indicated by a wavy line (Fig. 9).

When the carbon atom of the carbonyl group is involved in ring formation, leading to hemiacetal (pyranose or furanose ring) development, it becomes chiral. With D-sugars, the configuration that has the hydroxyl group located below the ring is the alpha form. For example, therefore, \(-D\)-glucopyranose is D-glucose in the pyranose (six-membered) ring from with the configuration of the new chiral carbon atom, C-1, termed the anomeric carbon atom, alpha. When the newly formed hydroxyl group at C-1 is above the ring, it is in the beta position, and the structure is named \(b\)-D-glucopyranose. This designation holds for all D-sugars. For sugars in the L-series, the opposite is true—that is, the anomeric hydroxyl group is up in the alpha anomer and down in the beta anomer. *(See, for example, Fig. 8.)* This is so because, for example, \(-D\)-glucopyranose and \(-L\)-glucopyranose are mirror images of one another.

However, pyranose rings are not flat with the attached groups sticking straight up and straight down as the Haworth structure suggests. Rather, they occur in a variety of shapes (conformations), most commonly in one of two chair conformations, so called because they are shaped somewhat like a chair. In this shape, one bond on each carbon atom does project either up or down from the ring; these are called axial bonds or axial positions. The other bond not involved in ring formation is either up or down with respect to the axial bonds but with respect to the ring projects out around the perimeter in what is called an equatorial position (Fig. 10).

Using \(-D\)-glucopyranose as an example, C-2, C-3, C-5, and the ring oxygen atom remain in a plane, but C-4 is raised slightly above the plane and C-1 is positioned slightly below the plane as in Figures 10 and 11. This conformation is designated \(^4C_1\). The notation C indicates that the ring is chair-shaped; the superscript and subscript numbers indicate that C-4 is above the plane of the ring and C-1 below the plane. There are two chair forms. The second, \(^1C_4\), has

\*The \(-D\) and \(-L\) ring forms of a sugar are known as anomers. The two anomers comprise an anomeric pair.
all the axial and equatorial groups reversed. The six-membered ring distorts the normal carbon and oxygen atom bond angles less than do rings of other sizes. The strain is further lessened when the bulky hydroxyl groups are separated maximally from each other by the ring conformation that arranges the greatest number of them in equatorial rather than axial positions. The equatorial position is energetically favored, and rotation of carbon atoms takes place on their connecting bonds to swivel the bulky groups to equatorial positions in so far as possible.

As noted, \(\alpha\)-D-glucopyranose has all its hydroxyl groups in the equatorial arrangement, but each is bent either slightly above or slightly below the true equatorial position. In \(\alpha\)-D-glucopyranose, the hydroxyl group, all of which are in an equatorial position, alternate in an up-and-down arrangement, with that at C-1 positioned slightly up, that on C-2 slightly down, and continuing with an up-and-down arrangement. The bulky hydroxymethyl group, C-6 in hexoses, is almost always in a sterically free equatorial position. If \(\alpha\)-D-glucopyranose were in a

\[\text{D-Glucopyranose}\]

\[\text{\(\alpha\)-D-Glucopyranose} \quad \text{\(\beta\)-D-Glucopyranose}\]

\[\text{FIGURE 9}\]

D-Glucopyranose as a mixture of two chiral forms.
1C₁ conformation, all the bulky groups would be axial; so very little D-glucopyranose exists in the 1C₁ conformation, a much higher energy form.

Six-membered sugar rings are than quite stable if bulky groups, such as hydroxyl groups and the hydroxymethyl group, are in equatorial positions. Thus, D-glucopyranose dissolves in water to give a rapidly equilibrating mixture containing the open chain form and its five, six-, and seven-membered ring forms. At room temperature, the six-membered (pyranose) ring forms predominate, followed by the five-membered (furanose) ring forms and only a trace of the seven-membered ring forms. The anomeric arrangement of each ring may be alpha or beta. The open-chain, aldehydo form constitutes only about 0.003% of the total forms (Fig. 12).

4.1.3 Glycosides

The hemiacetal form of sugars can react with an alcohol to produce a full acetal, called a glycoside. The acetal linkage at the anomeric carbon atom is indicated by the -ide ending. In the case of D-glucose reacting with methanol, the product is mainly methyl D-glucopyranoside, with less methyl D-glucopyranoside (Fig. 13).

The two anomeric forms of the five-membered-ring furanosides are also formed, but being higher energy structures, they reorganize into more stable forms and are present at equilibrium in comparatively low quantities. The methyl group in this case, and any other group bonded to a sugar to make a glycoside, is termed an aglycon. Glycosides undergo hydrolysis to yield a reducing sugar (see Sec. 4.1.4.1) and a hydroxylated compound in the presence of warm or hot aqueous acid.

4.1.4 Monosaccharide Reactions

All carbohydrate molecules have hydroxyl groups available for reaction. Simple monosaccharide and most other low-molecular-weight carbohydrate molecules also have carbonyl groups available for reaction. Formation of pyranose and furanose rings (cyclic hemiacetals) and of glycosides (acetals) of Monosaccharides has already been presented.
4.1.4.1 Oxidation to Aldonic Acids and Aldonolactones

Aldoses are readily oxidized to aldonic acids. The reaction is commonly used for quantitative determination of sugars. One of the earliest methods for quantitative measurement of sugars employed Fehling solution. Fehling solution is an alkaline solution of copper(II) that oxidizes an aldose to an aldonate and in the process is reduced to copper(I), which precipitates as brick-red Cu₂O. Variations, the Nelson-Somogyi and Benedict reagents, are still used for determining amounts of reducing sugars in foods and other biological materials.
Because, in the process of oxidizing the aldehyde group of an aldose to the salt of a carboxylic acid group, the oxidizing agent is reduced, aldoses are called reducing sugars. Ketoses are also termed reducing sugars because, under the alkaline conditions of the Fehling test, ketoses are isomerized to aldoses. Benedict reagent, which is not alkaline, will react with aldoses but not with ketoses.

A simple and specific method for quantitative oxidation of \( \text{D}-\text{glucose} \) to \( \text{D}-\text{gluconic acid} \) uses the enzyme glucose oxidase, with the initial product being the 1,5,6-lactone (an intramolecular ester) of the acid (Fig. 14). The reaction is commonly employed to measure the amount of \( \text{D}-\text{glucose} \) in foods and other biological materials, including the \( \text{D}-\text{glucose} \) level of blood. \( \text{D}-\text{Gluconic acid} \) is a natural constituent of fruit juices and honey.

The reaction given in Figure 14 is also used for the manufacture of commercial \( \text{D}-\text{gluconic acid} \) and its lactone. \( \text{D}-\text{Glucono-delta-lactone (GDL), D-glucono-1,5-lactone} \) according to systematic nomenclature, hydrolyzes to completion in water in about 3 hr at room temperature, effecting a decrease in pH. Its slow hydrolysis, slow acidification, and mild taste set GDL apart from other food acidulants. It is used in meats and dairy products, but particularly in baked goods as a component of chemical leavening agents for preleavened products.

4.1.4.2 Reduction of Carbonyl Groups [9]

Hydrogenation is the addition of hydrogen to a double bond. When applied to carbohydrates, it most often entails addition of hydrogen to the double bond between the oxygen atom and the carbon atom of the carbonyl group of an aldose or ketose. Hydrogenation of \( \text{D}-\text{glucose} \) is easily accomplished with hydrogen gas under pressure in the presence of Raney nickel. The product is \( \text{D}-\text{glucitol} \), commonly known as sorbitol, where the -itol suffix denotes a sugar alcohol (an alditol) (Fig. 15). Alditols are also known as polyhydroxy alcohols and as polyols. Because it is derived from a hexose, \( \text{D}-\text{glucitol} \) (sorbitol) is specifically a hexitol. It is found widely distributed throughout the plant world, ranging from algae to higher orders where it is found in fruits and berries, but the amounts present are generally small. It is 50% as sweet as sucrose, is sold both as a syrup and as crystals, and is used as a general humectant.

\( \text{D}-\text{Mannitol} \) can be obtained by hydrogenation of \( \text{D}-\text{mannose} \). Commercially, it is obtained along with sorbitol from hydrogenolysis of sucrose. It develops from hydrogenation of the \( \text{D}-\text{fructose} \) component of sucrose and from isomerization of \( \text{D}-\text{glucose} \), which can be controlled

\[
2\text{Cu(OH)}_2 + \text{R-C} = \overset{\text{O}}{\text{O}} \rightarrow \text{R-C-\text{OH}} + \text{Cu}_2\text{O} + \text{H}_2\text{O}
\] (1)

**FIGURE 14**

Oxidation of \( \text{D}-\text{glucose} \) catalyzed by glucose oxidase.
by the alkalinity of the solution undergoing catalytic hydrogenation (Fig. 16). D-Mannitol, unlike sorbitol, is not a humectant. Rather, it crystallizes easily and is only moderately soluble. It has been used as a nonsticky coating on candies. It is 65% as sweet as sucrose and is used in sugar-free chocolates, pressed mints, cough drops, and hard and soft candies.

Xylitol (Fig. 17) is produced from hydrogenation of D-xylene obtained from hemicelluloses, especially from birch trees. Its crystals have an endothermic heat of solution and give a cool feel when placed in the mouth. It is used in dry hard candies and in sugarless chewing gum. It is about 70% as sweet as sucrose. When xylitol is used in place of sucrose, there is a reduction in dental caries because xylitol is not metabolized by the microflora of the mouth to produce plaques.

4.1.4.3 Uronic Acids

The terminal carbon atom (at the other end of the carbon chain from the aldehyde group) of a monosaccharide unit of an oligo- or polysaccharide may occur in an oxidized (carboxylic acid) form. Such an aldohexose with C-6 in the form of a carboxylic acid group is called a uronic acid. When the chiral carbon atoms of a uronic acid are in the same configuration as they are in D-galactose, for example, the compound is D-galacturonic acid (Fig. 18), the principal component of pectin (see Sec. 4.10).
4.1.4.4 Hydroxyl Group Esters

The hydroxyl groups of carbohydrates, like the hydroxyl groups of simple alcohols, form esters with organic and some inorganic acids. Reaction of hydroxyl groups with a carboxylic acid anhydride or chloride (an acyl chloride) in the presence of a suitable base produces an ester.

\[
\text{ROH} + R'\text{C}O\text{C}-R' \text{ or } R'\text{C}-\text{Cl} \rightarrow \text{R-O-C}-R' + \text{HO-C-R' or HCl}
\]

(2)

Acetates, succinate half-esters, and other carboxylic acid esters of carbohydrates occur in nature. They are found especially as components of polysaccharides. Sugar phosphates are common metabolic intermediates (Fig. 19).

Monoesters of phosphoric acid are also found as constituents of polysaccharides. For example, potato starch contains a small percentage of phosphate ester groups. Corn starch contains even less. In producing modified food starch, corn starch is often derivatized with one or the other or both of mono- and distarch ester groups (see Sec. 4.4.9). Other esters of starch, most notably the acetate, succinate and substituted succinate half-esters, and distarch adipates, are in the class of modified food starches (see Sec. 4.4.9). Sucrose (see Sec. 4.2.3) fatty acid esters are produced commercially as emulsifiers. Members of the family of red seaweed polysaccharides, which includes the carrageenans (see Sec. 4.8), contain sulfate groups (half-esters of sulfuric acid, R-\text{OSO}_3^-).

4.1.4.5 Hydroxyl Group Ethers

The hydroxyl groups of carbohydrates, like the hydroxyl groups of simple alcohols, can from ethers as well as esters. Ethers of carbohydrates are not as common in nature as are esters. However, polysaccharides are etherified commercially to modify their properties and make them more useful. Examples are the production of methyl (\text{-O-CH}_3), sodium carboxy-
methyl (-O-CH₂-CO₂⁺ Na⁺), and hydroxypropyl (-O-CH₂-CHOH-CH₃) ethers of cellulose and hydroxypropyl ethers of starch, all of which are approved for food use.

A special type of ether, an internal ether formed between carbon atoms 3 and 6 of a D-galactosyl unit, is found in the red seaweed polysaccharides, specifically agar, furcellaran, kappa-carrageenan, and iota-carrageenan (see Sec. 4.8) (Fig. 20). Such an internal ether is known
as a 3,6-anhydro ring, whose name derives from the fact that the elements of water (HOH) are removed during its formation.

A series of nonionic surfactants based on sorbitol (D-glucitol) is used in foods as water-in-oil emulsifiers and as defoamers. They are produced by esterification of sorbitol with fatty acids. Cyclic dehydration accompanies esterification (primarily at a primary hydroxyl group, i.e., C-1 or C-6) so that the carbohydrate (hydrophilic) portion is not only sorbitol but also its mono- and dianhydrides (cyclic ethers). The products are known as sorbitan esters (Fig. 21). The product called sorbitan monostearate is actually a mixture of partial stearic (C_{18}) and palmitic (C_{16}) acid esters of sorbitol (D-glucitol), 1,5-anhydro-D-glucitol (1,5-sorbitan), 1,4-anhydro-D-glucitol (1,4-sorbitan), both internal (cyclic) ethers, and 1,4:3,6-dianhydro-D-glucitol (isosorbide), an internal dicyclic ether. Sorbitan fatty acid esters, such as sorbitan monostearate, sorbitan monolaurate, and sorbitan monooleate, are sometimes modified by reaction with ethylene oxide to produce so-called ethoxylated sorbitan esters, also nonionic detergents approved by the FDA for food use.

4.1.4.6 Nonenzymic Browning \[10,12,30,59\]

Under some conditions, reducing sugars produce brown colors that are desirable and important in some foods. Other brown colors obtained upon heating or during long-term storage of foods containing reducing sugars are undesirable. Common browning of foods on heating or on storage is usually due to a chemical reaction between reducing sugars, mainly D-glucose, and a free amino acid or a free amino group of an amino acid that is part of a protein chain. This reaction is called the Maillard reaction. It is also called nonenzymic browning to differentiate it from the often rapid, enzyme-catalyzed browning commonly observed in freshly cut fruits and vegetables, such as apples and potatoes.

When aldoses or ketoses are heated in solution with amines, a variety of reactions ensue, producing numerous compounds, some of which are flavors, aromas, and dark-colored polymeric materials, but both reactants, disappear only slowly. The flavors, aromas, and colors may be either desirable or undesirable. They may be produced by frying, roasting, baking, or storage.

The reducing sugar reacts reversibly with the amine to produce a glycosylamine, as illustrates with D-glucose (Fig. 22). This undergoes a reaction called the Amadori rearrangement to give, in the case of D-glucose, a derivative of 1-amino-1-deoxy-D-fructose. Reaction continues, especially at pH 5 or lower, to give an intermediate that dehydrates. Eventually a furan derivative is formed; that from a hexose is 5-hydroxymethyl-2-furaldehyde (HMF) (Fig. 23). Under less acidic conditions (higher than pH 5), the reactive cyclic compounds (HMF and others) polymerize quickly to a dark-colored, insoluble material containing nitrogen.

Maillard browning products, including soluble and insoluble polymers, are found where reducing sugars and amino acids, proteins, and/or other nitrogen-containing compounds are heated together, such as in soy sauce and bread crusts. Maillard reaction products are important contributors to the flavor of milk chocolate. The Maillard reaction is also important in the production of caramels, toffees, and fudges, during which reducing sugars also react with milk
Proteins. D-Glucose undergoes the browning reaction faster than does D-fructose. Application of heat is generally required for nonenzymic browning. While Maillard reactions are useful, they also have a negative side. Reaction of reducing sugars with amino acids destroys the amino acid. This is of particular importance with l-lysine, an essential amino acid whose -amino group can react when the amino acid is part of a protein molecule. Also, a relationship has been found between formation of mutagenic compounds and cooking of protein-rich foods. Mutagenic heterocyclic amines have been isolated from broiled and fried meat and fish, and from beef extracts.

Heating of carbohydrates, in particular sucrose (see Sec. 4.2.3) and reducing sugars, without nitrogen-containing compounds effects a complex group of reactions termed caramelization. Reaction is facilitated by small amounts of acids and certain salts. Mostly thermolysis causes dehydration of the sugar molecule with introduction of double bonds or formation of anhydro rings. Introduction of double bonds leads to unsaturated rings such as furans. Conjugated double bonds absorb light and produce color. Often unsaturated rings will condense to polymers yielding useful colors. Catalysts increase the reaction rate and are often used to direct the reaction to specific types of caramel colors, solubilities, and acidities.

Brown caramel color made by heating a sucrose (see Sec. 4.2.3) solution with ammonium bisulfite is used in cola soft drinks, other acidic beverages, baked goods, syrups, candies, pet
foods, and dry seasonings. Its solutions are acidic (pH 2–4.5) and contain colloidal particles with negative charges. The acidic salt catalyzes cleavage of the glycosidic bond of sucrose; the ammonium ion participates in the Amadori rearrangement. Another caramel color, also made by heating sugar with ammonium salts, is reddish brown, imparts pH values of 4.2–4.8 to water, contains colloidal particles with positive charges, and is used in baked goods, syrups, and puddings. Caramel color made by heating sugar without an ammonium salt is also reddish brown, but contains colloidal particles with slightly negative charges and has a solution pH of 3–4. It is used in beer and other alcoholic beverages. The nonenzymic browning caramel pigments are large polymeric molecules with complex, variable, and unknown structures. It is these polymers that form the colloidal particles. Their rate of formation increases with increasing temperature and pH.

Certain pyrolytic reactions of sugars (Fig. 24) produce unsaturated ring systems that have unique flavors and fragrances in addition to the coloring materials. Maltol (3-hydroxy-2-methylpyran-4-one) and isomaltol (3-hydroxy-2-acetylfuran) contribute to the flavor of bread. 2H-4-Hydroxy-5-methylfuran-3-one can be used to enhance various flavors and sweeteners.
4.2 Oligosaccharides

An oligosaccharide contains 2 to 20 sugar units joined by glycosidic bonds. When a molecule contains more than 20 units, it is a polysaccharide.

Disaccharides are glycosides in which the aglycon is a monosaccharide unit. A compound containing three monosaccharide units is a trisaccharide. Structures containing from 4 to 10 glycosyl units, whether linear or branched, are tetra-, penta-, hexa-, octa-, nona-, and decasaccharides, and so on.

Because glycosidic bonds are part of acetal structures, they undergo acid-catalyzed hydrolysis, that is, cleavage in the presence of aqueous acid and heat. Only a few oligosaccharides occur in nature. Most are produced by hydrolysis of polysaccharides into smaller units.

4.2.1 Maltose

Maltose (Fig. 25), which can be obtained by hydrolysis of starch, is an example of a disaccharide. The end unit on the right (as customarily written) has a potentially free aldehyde group; therefore, it is the reducing end and will be in equilibrium with alpha and beta six-membered ring forms, as described earlier for monosaccharides. Since O-4 is blocked by attachment of the second D-glucopyranosyl unit, a furanose ring cannot form. Maltose is a reducing sugar because its aldehyde group is free to react with oxidants and, in fact, to undergo almost all reactions as though it were present as a free aldose.

Maltose is readily produced by hydrolysis of starch using the enzyme \( \beta \)-amylase (see Sec. 4.4.8). It occurs only rarely in plants, and even then, it results from partial hydrolysis of starch. Maltose is produced during malting of grains, especially barley, and commercially by the specific enzyme-catalyzed hydrolysis of starch using \( \beta \)-amylase from Bacillus bacteria, although the \( \beta \)-amylases from barley seed, soybeans, and sweet potatoes may be used. Maltose is used sparingly as a mild sweetner for foods.
4.2.2 lactose

The disaccharide lactose (Fig. 26) occurs in milk, mainly free, but to a small extent as a component of higher oligosaccharides. The concentration of lactose in milk varies with the mammalian source from 2.0 to 8.5%. Cow and goat milks contain 4.5–4.8%, and human milk about 7%. Lactose is the primary carbohydrate source for developing mammals. In humans, lactose constitutes 40% of the energy consumed during nursing. Utilization of lactose for energy must be preceded by hydrolysis to the constituent monosaccharides, D-glucose and D-galactose. Milk also contains 0.3–0.6% of lactose-containing oligosaccharides, many of which are important as energy sources for growth of a specific variant of *Lactobacillus bifidus*, which, as a result, is the predominant microorganism of the intestinal flora of breast-fed infants.

Lactose is ingested in milk and other unfermented dairy products, such as ice cream. Fermented dairy products, such as most yogurt and cheese, contain less lactose because during fermentation some of the lactose is converted into lactic acid. Lactose stimulates intestinal adsorption and retention of calcium. Lactose is not digested until it reaches the small intestine, where the hydrolytic enzyme lactase is located. Lactase (α-D-galactosidase) is a membrane-bound enzyme located in the brush border epithelial cells of the small intestine. It catalyzes the hydrolysis of lactose into its constituent monosaccharides, D-glucose and D-galactose. Of the carbohydrates, only monosaccharides are absorbed from the intestines. Both D-glucose and D-galactose are rapidly absorbed and enter the blood stream.

\[
\text{lactose} \xrightarrow{\text{lactase}} \text{D-glucose} + \text{D-galactose} \tag{3}
\]

If for some reason the ingested lactose is only partially hydrolyzed, that is, only partially digested, or is not hydrolyzed at all, a clinical syndrome called lactose intolerance results. If there is a deficiency of lactase, some lactose remains in the lumen of the small intestine. The presence of lactose tends to draw fluid into the lumen by osmosis. This fluid produces abdominal distention and cramps. From the small intestine, the lactose passes into the large intestine (colon) where it undergoes anaerobic bacterial fermentation to lactic acid (present as the lactate anion) and other short-chain acids (Fig. 27). The increase in the concentration of molecules, that is, the increase in osmolality, results in still greater retention of fluid. In addition, the acidic products of fermentation lower the pH and irritate the lining of the colon, leading to an increased movement of the contents. Diarrhea is caused both by the retention of fluid and the increased movement of the intestinal contents. The gaseous products of fermentation cause bloating and cramping.

Lactose intolerance is not usually seen in children until after about 6 years of age. At this
point, the incidence of lactose-intolerant individuals beings to rise and increases throughout the life span, with the greatest incidence in the elderly. Both the incidence and the degree of lactose intolerance vary by ethnic group, indicating that the presence or absence of lactase is under genetic control.

There are two ways to overcome the effects of lactase deficiency. One is to remove the lactose by fermentation; that produces yogurt and buttermilk products. Another is to produce reduced-lactose milk by adding lactase to it. However, both products of hydrolysis, D-glucose and D-galactose, are sweeter than lactose, and at about 80% hydrolysis, the taste change becomes too evident. Therefore, most reduced-lactose milk has the lactose reduced as close as possible to the 70% government-mandated limit for a claim. In a technology under development, live yogurt cultures are added to refrigerated milk. The bacteria remain dormant in the cold and do not change the flavor of the milk, but upon reaching the small intestine, release lactase.

Other carbohydrates that are not completely broken down into monosaccharides by intestinal enzymes and are not absorbed also pass into the colon. There they also are metabolized by microorganisms, producing lactate and gas. Again diarrhea and bloating result. This problem can occur from eating beans, because beans contain a trisaccharide (raffinose) and a tetrasaccharide (stachyose) (see Sec. 4.2.3) that are not hydrolyzed to monosaccharides by intestinal enzymes and thus pass into the colon, where they are fermented.

4.2.3 Sucrose [35,39]

The per person daily utilization of sucrose, usually called simply sugar or table sugar, in the United States averages about 160 g, but sucrose is also used extensively in fermentations, in bakery products where it is also largely used up in fermentation, and in pet food, so the actual average daily amount consumed by individuals in foods and beverages in about 55 g (20 kg or 43 lb/year). Sucrose is composed of an D-glucopyranosyl unit and a β-D-fructofuranosyl unit linked head to head (reducing end to reducing end) rather than by the usual head-to-tail linkage (Fig. 28). Since it has no reducing end, it is a nonreducing sugar.

There are two principal sources of commercial source—sugar cane and sugar beets. Also present in sugar beet extract are a trisaccharide, raffinose, which has a D-galactopyranosyl unit attached to sucrose, and a tetrasaccharide, stachyose, which contains another D-galactosyl unit (Fig. 29). These oligosaccharides are also found in beans, are nondigestible, and are the source of the flatulence associated with eating beans.

Commercial brown sugar is made by treating white sugar crystals with molasses to leave a coating of desired thickness. Grades range from light yellow to dark brown. Confection, or
powdered, sugar is pulverized sucrose. It usually contains 3% corn starch as an antickaking agent. To make fondant sugar, which is used in icings and confections, very fine sucrose crystals are surrounded with a saturated solution of invert sugar, corn syrup, or maltodextrin.*

For many food product applications, sucrose is not crystallized; rather, it is shipped as a refined aqueous solution known as liquid sugar. Sucrose and most other low-molecular-weight carbohydrates (for example, monosaccharides, alditols, disaccharides, and other low-molecular-weight oligosaccharides), because of their great hydrophilicity and solubility, can form highly concentrated solutions of high osmolality. Such solutions, as exemplified by pancake and waffle syrups and honey, need no preservatives themselves and can be used not only as sweeteners (although not all such carbohydrate syrups need have much sweetness) but also as preservatives and humectants.

A portion of the water in any carbohydrate solution is nonfreezable. When the freezable water crystallizes, that is, forms ice, the concentrations of solute in the remaining liquid phase increases, and the freezing point decreases. There is a consequential increase in viscosity of the remaining solution. Eventually, the liquid phase solidifies as a glass in which the mobility of all molecules becomes greatly restricted and diffusion-dependent reactions become very slow.

\[
\alpha\text{Gal}(1\rightarrow 6)\alpha\text{Gal}(1\rightarrow 6)\alpha\text{Glc}(1\rightarrow 2)\text{fruf}
\]

\[
\begin{align*}
\text{sucrose} \\
\text{raffinose} \\
\text{stachyose}
\end{align*}
\]

*See Section 4.4.8 for a description of the latter two products. Invert sugar is the equimolar mixture of D-glucose and D-fructose formed by hydrolysis of sucrose.
(see Chap. 2); because of the restricted motion, these glass-state water molecules cannot crystallize. In this way, carbohydrates function as cryoprotectants and protect against the dehydration that destroys structure and texture caused by freezing.

The sucrase of the human intestinal tract catalyzes hydrolysis of sucrose into \(\text{D}-\text{glucose}\) and \(\text{D}-\text{fructose}\), making sucrose one of the three carbohydrates (other than monosaccharides) humans can utilize for energy, the other two being lactose and starch. Monosaccharides (\(\text{D}-\text{glucose}\) and \(\text{D}-\text{fructose}\) being the only significant ones in our diets) do not need to undergo digestion before absorption.

4.3 Polysaccharides [42,47,55]

Polysaccharides are polymers of monosaccharides. Like the oligosaccharides, they are composed of glycosyl units in linear or branched arrangements, but most are much larger than the 20-unit limit of oligosaccharides. The number of monosaccharide units in a polysaccharide, termed its degree of polymerization (DP), varies. Only a few polysaccharides have a DP less than 100; most have DPs in the range 200–3000. The larger ones, like cellulose, have a DP of 7000–15,000. It is estimated that more than 90% of the considerable carbohydrate mass in nature is in the form of polysaccharides. Polysaccharides can be either linear or branched. The general scientific term for polysaccharides is glycans.

If all the glycosyl units are of the same sugar type, they are homogeneous as to monomer units and are called homoglycans. Examples of homoglycans are cellulose (see Sec. 4.5) and starch amyllose (see Sec. 4.4.1), which are linear, and starch amylopectin (see Sec. 4.4.2), which is branched. All three are composed only of \(\text{D}-\text{glucopyranosyl}\) units.

When a polysaccharide is composed of two or more different monosaccharide units, it is a heteroglycan. A polysaccharide that contains two different monosaccharide units is diheteroglycan, a polysaccharide that contains three different monosaccharide units is a triheteroglycan, and so on. Diheteroglycans generally are either linear polymers of blocks of similar units alternating along the chain, or consist of a linear chain of one type of glycosyl unit with a second present as single-unit branches. Examples of the former type are algins (see Section 4.9) and of the latter guar and locust bean gums (see Sec. 4.6).

In the shorthand notations of oligo-and polysaccharides, the glycosyl units are designated by the first three letters of their names with the first letter being capitalized, except for glucose, which is \(\text{Glc}\). If the monosaccharide unit is that of a \(\text{D}\)-sugar, the \(\text{D}\) is omitted; only \(\text{L}\) sugars are so designated, such as \(\text{L\text{-Ara}}\). The size of the ring is designated by an italicized \(p\) for pyranosyl or \(f\) for furanosyl. The anomic configuration is designated with \(a\) or \(b\) as appropriate; for example, an \(-\text{D-glucopyranosyl}\) unit is indicated as \(\text{Glc}\). Uronic acids are designated with a capital \(A\); for example, an \(\text{L-gulopyranosyluronic acid}\) unit (see Sec. 4.9) is indicated as \(\text{LGulA}\). The position of linkages are designated either as, for example, \(\text{1}\rightarrow3\) or \(1,3\), with the latter being more commonly used by biochemists and the former more commonly used by carbohydrate chemists. Using the shorthand notation, the structure of lactose is represented as \(\text{bGalp(1}\rightarrow4\text{Glc)}\) or \(\text{bGalp1,4Glc}\) and maltose as \(\text{Glc}\text{p1,4Glc)}\) or \(\text{Glc1,4Glc}\). (Note that the reducing end cannot be designated as \(a\) or \(b\) as pyranose or furanose because the ring can open and close; that is, in solutions of lactose and maltose and other oligo-and polysaccharides, the reducing end unit will occur as a mixture of \(-\text{a-}\) and \(-\text{b-}\)pyranose ring forms and the acyclic form, with rapid interconversion between them; see Fig. 12.)
4.3.1 Polysaccharide Solubility

Most polysaccharides contain glycosyl units that, on average, have three hydroxyl groups. Polysaccharides are thus polyols in which each hydroxyl group has the possibility of hydrogen bonding to one or more water molecules. Also, the ring oxygen atom and the glycosidic oxygen atom connecting one sugar ring to another can form hydrogen bonds with water. With every sugar unit in the chain having the capacity to hold water molecules avidly, glycans possess a strong affinity for water and readily hydrate when water is available. In aqueous systems, polysaccharide particles can take up water, swell, and usually undergo partial or complete dissolution.

Polysaccharides modify and control the mobility of water in food systems, and water plays an important role in influencing the physical and functional properties of polysaccharides. Together polysaccharides and water control many functional properties of foods, including texture.

The water of hydration that is naturally hydrogen-bonded to and thus solvates polysaccharide molecules is often described as water whose structure has been sufficiently modified by the presence of the polymer molecule so that it will not freeze. The water has also been referred to as plasticizing water. The molecules that make up this water are not energetically bound in a chemical sense. While their motions are retarded, they are able to exchange freely and rapidly with other water molecules. This water of hydration makes up only a small part of the total water in gels and fresh tissue foods. Water in excess of the hydration water is held in capillaries and cavities of various sizes in the gel or tissue.

Polysaccharides are cryostabilizers rather than cryoprotectants, because they do not increase the osmolality or depress the freezing point of water significantly, since they are large, high-molecular-weight molecules and these are colligative properties. As an example, when a starch solution is frozen, a two-phase system of crystalline water (ice) and a glass consisting of about 70% starch molecules and 30% nonfreezable water is formed. As in the case of solutions of low-molecular-weight carbohydrates, the nonfreezable water is part of a highly concentrated polysaccharide solution in which the mobility of the water molecules is restricted by the extremely high viscosity. However, while most polysaccharides provide cryostabilization by producing this freeze-concentrated matrix, which severely limits molecular mobility, there is evidence that others provide cryostabilization by restricting ice crystal growth by adsorption to nuclei or active crystal growth sites. Other polysaccharides may be ice nucleators.

Thus both high- and low-molecular-weight carbohydrates are generally effective in protecting food products stored at freezer temperatures (typically -18°C) from destructive changes in texture and structure. In both cases, the improvement in product quality and storage stability is a result of controlling both the amount (particularly in the case of low-molecular-weight carbohydrates) and the structural state (particularly in the case of polymeric carbohydrates) of the freeze-concentrated, amorphous matrix surrounding ice crystals.

Most, if not all, polysaccharides, except those with very bushlike, branch-on-branch structures, exist in some sort of helical shape. Certain linear homoglycans, like cellulose (see Sec. 4.5), have flat, ribbon-like structures. Such uniform linear chains undergo hydrogen bonding with each other so as to form crystallites separated by amorphous regions. Crystalline arrangements of this sort are called fringed micelles (Fig. 30). It is these crystallites of linear chains that give cellulose fibers, like wood and cotton fibers, their great strength, insolvability, and resistance to breakdown, the latter because the crystalline regions are nearly inaccessible to
enzyme penetration. These highly ordered polysaccharides with orientation and crystallinity comprise the exception, rather than the rule. Most polysaccharides are not so crystalline as to impart water insolubility, but are readily hydrated and dissolved.

Most unbranched diheteroglycans containing nonuniform blocks of glycosyl units and most branched glycans cannot form micelles because chain segments are prevented from becoming closely packed over lengths necessary to form strong intermolecular bonding. Hence, these chains have a degree of solubility that increases as chains become less able to fit closely together. In general, polysaccharides become more soluble in proportion to the degree of irregularity of the molecular chains, which is another way of saying that, as the ease with which molecules fit together decreases, the solubility of the molecules increases.

Water-soluble polysaccharides and modified polysaccharides used in food and other industrial applications are known as gums or hydrocolloids. Gums are sold as powders of varying particle size.
4.3.2 Polysaccharide Solution Viscosity and Stability [13]

Polysaccharides (gums, hydrocolloids) are used primarily to thicken and/or gel aqueous solutions and otherwise to modify and/or control the flow properties and textures of liquid food and beverage products and the deformation properties of semisolid foods. They are generally used in food products at concentrations of 0.25–0.50%, indicating their great ability to produce viscosity and to form gels.

The viscosity of a polymer solution is a function of the size and shape of its molecules and the conformations they adopt in the solvent. In foods and beverages, the solvent is an aqueous solution of other solutes. The shapes of polysaccharide molecules in solution are a function of oscillations around the bonds of the glycosidic linkages. The greater the internal freedom at each glycosidic linkage, the greater the number of conformations available to each individual segment. Chain flexibility thus provides a strong entropic drive, which generally overcomes energy considerations and induces the chain to approach disordered or random coil states in solution (Fig. 31). However, most polysaccharides exhibit deviations from strictly random coil states, forming stiff coils, with the specific nature of the coils being a function of the monosaccharide composition and linkages, some being compact, some expanded.

Linear polymer molecules in solution gyrate and flex, sweeping out a large space. They frequently collide with each other, creating friction, consuming energy, and thereby producing viscosity. Linear polysaccharides produce highly viscous solutions, even at low concentrations. Viscosity depends both on the DP (molecular weight) and the extension and rigidity, that is, the shape and flexibility, of solvated polymer chain.

A highly branched polysaccharide molecule will sweep out much less space than a linear polysaccharide of the same molecular weight (Fig. 32). As a result, highly branched molecules will collide less frequently and will produce a much lower viscosity than will linear molecules of the same DP. This also implies that highly branched polysaccharide molecules must be significantly larger than linear polysaccharide molecules to produce the same viscosity at the same concentration.

Likewise, linear polysaccharide chains bearing only one type of ionic charge (always a negative charge derived from ionization of carboxyl or sulfate half-ester groups) assume an extended configuration due to repulsion of the like charges, increasing the end-to-end chain length and thus the volume swept out by the polymer. Therefore, these polymers tend to produce solutions of high viscosity.

FIGURE 31
Randomly coiled polysaccharide molecules.
Unbranched, regular glycans, which dissolve in water by heating, form unstable molecular dispersions that precipitate or gel rapidly. This occurs as segments of the long molecules collide and form intermolecular bonds over the distance of a few units. Initial short alignments then extend in a zipper-like fashion to greatly strengthen intermolecular associations. Other segments of other chains colliding with this organized nucleus bind to it, increasing the size of the ordered, crystalline phase. Linear molecules continue to bind to fashion a fringed micelle that may reach a size where gravitational forces cause precipitation. For example, starch amylose, when dissolved in water with the aid of heat followed by cooling the solution, undergoes molecular aggregation and precipitates, a process called retrogradation. During cooling of bread and other baked products, amylose molecules associate to produce a firming. Over a longer storage time, the branches of amylpectin associate to produce staling (see Sec. 4.4.6).

In general, molecules of all unbranched, neutral homoglycans have an inherent tendency to associate and partially crystallize. However, if linear glycans are derivatized, or occur naturally derivatized, as does guar gum (see Sec. 4.6), which has single-unit glycosyl branches along a backbone chain, their segments are prevented from association and stable solutions result.

Stable solutions are also formed if the linear chains contain charged groups where coulombic repulsions prevent segments from approaching each other. As already mentioned, charge repulsion also causes chains to extend, which provides high viscosities. Such highly viscous, stable solutions are seen with sodium alginate (see Sec. 4.9), where each glycosyl unit is a uronic acid unit having a carboxylic acid group in the salt form, and in xanthan (see Sec. 4.7), where one out of five glycosyl units is a uronic acid unit and another carboxylate group may be present. But if the pH of an alginate solution is lowered to 3, where ionization of carboxylic acid groups is somewhat repressed because the $pK_a$ values of the constituent monomers are 3.38 and 3.65, the resulting less ionic molecules can associate and precipitate or form a gel as expected for unbranched, neutral glycans.
Carrageenans are mixtures of linear chains that have a negative charge due to numerous ionized sulfate half-ester groups along the chain (see Sec. 4.8). These molecules do not precipitate at low pH because the sulfate group remains ionized at all practical pH values.

Solutions of gums are dispersions of hydrated molecules and/or aggregates of hydrated molecules. Their flow behavior is determined by the size, shape, ease of deformation (flexibility), and presence and magnitude of charges on these hydrated molecules and/or aggregates. There are two general kinds of flow exhibited by polysaccharide solutions: pseudoplastic (by far the most common) and thixotropic.

Pseudoplastic fluids are shear-thinning. In pseudoplastic flow, a more rapid increase in flow results from an increase in shear rate; that is, the faster a fluid flows, the less viscous it becomes (Fig. 33). The flow rate can be increased by increasing the applied force by pouring, chewing, swallowing, pumping, mixing, etc. The change in viscosity is independent of time; that is, the rate of flow changes instantaneously as the shear rate is changed. Linear polymer molecules form shear-thinning, usually pseudoplastic, solutions. In general, higher molecular weight gums are more pseudoplastic.

Gum solutions that are less pseudoplastic are said to give long flow; such solutions are generally perceived as being slimy. More pseudoplastic solutions are described as having short flow and are generally perceived as being nonslimy. In food science, a slimy material is one that is thick, coats the mouth, and is difficult to swallow. Sliminess is inversely related to pseudoplasticity; that is, to be perceived as being nonslimy, there must be marked thinning at the low shear rates produced by chewing and swallowing.

Thixotropic flow is a second type of shear-thinning flow. In this case, the viscosity reduction that results from an increase in the rate of flow does not occur instantaneously. The viscosity of thixotropic solutions decreases under a constant rate of shear in a time-dependent manner and regains the original viscosity after cessation of shear, but again only after a clearly

---

*“Short flow” is exhibited by shear-thinning, primarily pseudoplastic, viscous solutions and “long flow” by viscous solutions that exhibit little or no shear thinning. These terms were applied long before there were instruments to determine and measure rheological phenomena. They were arrived at in this way. When a gum or starch solution is allowed to drain from a pipette or a funnel, those that are not shear-thinning come out in long strings, while those that shear-thin form short drops. The latter occurs because, as more and more fluid exists the orifice, the weight of the string becomes greater and greater, which causes it to flow faster and faster, which causes it to shear-thin to the point that the string breaks into drops.
defined and measured time interval. This behavior is due to a gel $\rightarrow$ solution $\rightarrow$ gel transition. In other words, a thixotropic solution is at rest a weak (pourable) gel (see Sec. 4.3.3).

For solutions of most gums, an increase in temperature results in a decrease in viscosity. (Xanthan gum is an exception between 0 and 100°C; sec Sec. 4.7.) This is often an important property, for it means that higher solids can be put into solution at a higher temperature; then the solution can be cooled for thickening.

**4.3.3 Gels [6,18]**

A gel is a continuous, three-dimensional network of connected molecules or particles (such as crystals, emulsion droplets, or molecular aggregates/fibrils) entrapping a large volume of a continuous liquid phase, much as does a sponge. In many food products, the gel network consists of polymer (polysaccharide and/or protein) molecules or fibrils formed from polymer molecules joined in junction zones by hydrogen bonding, hydrophobic associations (van der Waals attractions), ionic cross bridges, entanglements, or covalent bonds, and the liquid phase is an aqueous solution of low-molecular-weight solutes and portions of the polymer chains.

Gels have some characteristics of solids and some of liquids. When polymer molecules or fibrils formed from polymer molecules interact over portions of their lengths to form junction zones and a three-dimensional network (Fig. 34), a fluid solution is changed into a material that

\[ \text{FIGURE 34} \]

A diagrammatic representation of the type of three-dimensional network structure found in gels. This type of structure is known as a fringed micelle structure. Parallel side-by-side chains indicate the ordered, crystalline structure of a junction zone. The holes between junction zones contain an aqueous solution of dissolved segments of polymer chains and other solutes.
has a sponge-like structure and can retain its shape. The three-dimensional network structure offers significant resistance to an applied stress causing it to behave in some respects as an elastic solid. However, the continuous liquid phase, in which molecules are completely mobile, makes a gel less stiff than an ordinary solid, causing it to behave in some respects as a viscous liquid. Therefore, a gel is a viscoelastic semisolid; that is, the response of a gel to stress is partly characteristic of an elastic solid and partly characteristic of a viscous liquid.

Although gel-like or salve-like materials can be formed by high concentrations of particles (much like tomato paste), to form a true gel, the polymer molecules or aggregates of molecules must first be in solution, then partially come out of solution in junction zone regions to form the three-dimensional gel network structure. In general, if junction zones grow larger after formation of the gel, the network becomes more compact, the structure contracts, and syneresis results. (The appearance of fluid droplets on the gel surface is called syneresis.)

Although polysaccharide gels generally contain only about 1% polymer—that is, they may contain as much as 99% water—they can be quite strong. Examples of polysaccharide gels are dessert gels, aspics, structured fruit pieces, structured onion rings, meat-analog pet foods, and icings.

Choice of a specific gum for a particular application depends on the viscosity or gel strength desired, desired rheology, pH of the system, temperatures during processing, interactions with other ingredients, desired texture, and cost of the amount needed to impart the desired properties. In addition, consideration is also given to desired functional characteristics. These include a gum's ability to function as a binder, bodying agent, bulking agent, crystallization inhibitor, clarifying agent, cloud agent, coating agent/film former, fat mimetic, flocculating agent, foam stabilizer, mold release agent, suspension stabilizer, swelling agent, syneresis inhibitor, and whipping agent and as an agent for water absorption and binding (water retention and migration control), adhesion, emulsification, emulsion stabilization, and encapsulation. Each food gum tends to have one or more outstanding unique property related to this list, and this property is often the basis for its choice (Table 2).

4.3.4 Polysaccharide Hydrolysis

Polysaccharides are relatively less stable to hydrolytic cleavage than are proteins and may, at times, undergo depolymerization during food processing and/or storage of foods. Often, food gums are deliberately depolymerized so a relatively high concentration can be used to provide body without producing undesirable viscosity.

Hydrolysis of glycosidic bonds joining monosaccharide (glycosyl) units in oligo- and polysaccharides can be catalyzed by either acids (H+) or enzymes. The extent of depolymerization, which has the effect of reducing viscosity, is determined by the acid strength, time, temperature, and structure of the polysaccharide. Generally, hydrolysis occurs most readily during thermal processing, because many foods are somewhat acidic. Defects associated with depolymerization during processing can usually be overcome by using more of the polysaccharide (gum) in the formulation to compensate for breakdown, using a higher viscosity grade of the gum, again to compensate for any depolymerization, or using a more acid-stable gum. Depolymerization can also be an important determinant of shelf life.

Polysaccharides are also subject to enzyme-catalyzed hydrolysis. The rate and end products of this process are controlled by the specificity of the enzyme, pH, time, and temperature. Polysaccharides, like any and all other carbohydrates, are subject to microbial attack because of their susceptibility to enzyme-catalyzed hydrolysis. Furthermore, gum products are very seldom delivered sterile, and this fact must be considered when using them as ingredients.
<table>
<thead>
<tr>
<th>Gum</th>
<th>Source</th>
<th>Class</th>
<th>General shape</th>
<th>Monomer units and linkages (approx. ratios)</th>
<th>Noncarbohydrate substituent groups</th>
<th>Water solubility</th>
<th>Key general characteristics</th>
<th>Major food applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxymethylcellulose (CMC)</td>
<td>Derived from cellulose</td>
<td>Modified cellulose</td>
<td>Linear</td>
<td>=&gt; (1-6) Glcp</td>
<td>Carboxymethyl other (DS 0.4-0.8)*</td>
<td>High</td>
<td>Clear, stable solutions that can be either pseudoplastic or thixotropic</td>
<td>Retarder of ice crystal growth in frozen dessert products</td>
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<td></td>
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<td></td>
<td>Thickener, suspending aid, protective colloid, and improver of mouthfeel, body, and texture in a variety of dressings, sauces and spreads</td>
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<td>Lubricant, film former, and processing aid for extruded products</td>
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<td></td>
<td></td>
<td>Batter thickener and humectant in cake and related mixes</td>
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<td></td>
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<td>Moisture binder and retarder of crystallization and/or syneresis in icings, frostings, toppings, fillings, and puddings</td>
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<td>Syrup thickener</td>
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<td>Suspending aid and thickener in dry powder, hot and cold drink mixes</td>
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<td>Gravy maker in dry pet food</td>
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<tr>
<td>Methylcellulose (MC) and hydroxypropylmethylcelluloses (HPMC)</td>
<td>Derived from cellulose</td>
<td>Modified cellulose</td>
<td>Linear</td>
<td>(\rightarrow 4)-(\beta)-GlcP</td>
<td>Hydroxypropyl (MS 0.02-0.3)* and methyl (DS 1.1-2.2)* ether groups</td>
<td>Soluble in cold water; insoluble in hot water</td>
<td>Clear solutions that are thermal gelling; surface active</td>
<td>MC: Provides fat-like characteristics. Reduces fat absorption in fried products. Imparts creaminess through film and viscosity formation. Provides lubricity. Gas retention during baking. Moisture retention and control of moisture distribution in bakery products (increases shelf life and imparts tenderness). HPMC: Non-dairy whipped toppings, where it stabilizes foams, improves whipping characteristics, prevents phase separation, and provides freeze-thaw stability.</td>
</tr>
<tr>
<td>Gum</td>
<td>Source Type</td>
<td>Class</td>
<td>General Shape</td>
<td>Monomer units and linkages</td>
<td>Noncarbohydrate substituent groups</td>
<td>Water solubility</td>
<td>Key general characteristics</td>
<td>Major food applications</td>
</tr>
<tr>
<td>---------------------</td>
<td>-------------------</td>
<td>-------------</td>
<td>------------------------</td>
<td>-----------------------------</td>
<td>-------------------------------------</td>
<td>-------------------</td>
<td>--------------------------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Xanthan gum</td>
<td>Fermentation</td>
<td>Saccharide</td>
<td>Linear with trisaccharide unit branches on every other main chain units (behaves as a linear polymer)</td>
<td>-4α-β-D-Glcp &amp; 1β-α-Manp</td>
<td>Acetyl ester Pyruvyl cyclic acetate</td>
<td>High</td>
<td>Very pseudoplastic, high viscosity solutions; excellent emulsion and suspension stabilizer; solution viscosity unaffected by temperature; solution viscosity unaffected by pH; excellent salt compatibility; synergistic increase in viscosity upon interaction with guar gum; heat reversible solution with LBG</td>
<td>Stabilization of dispersions, suspensions, and emulsions; Thickener</td>
</tr>
<tr>
<td>Carrageenan</td>
<td>Red algae</td>
<td>Seaweed</td>
<td>Sulfated half ester</td>
<td></td>
<td></td>
<td></td>
<td>Secondary stabilizer in ice cream and related products</td>
<td>Preparation of evaporated milk, instant formulas, freeze-thaw stable whipped cream, dairy desserts, and chocolate milk</td>
</tr>
<tr>
<td></td>
<td></td>
<td>extract</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Meat coating</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sulfated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Improves adhesion and increases water-holding capacity of meat emulsion products</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>gellan</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Improves texture and quality of low-fat meat products</td>
<td></td>
</tr>
</tbody>
</table>
Kappa types:

\[ \rightarrow \beta - \alpha \text{Galp} 4 - \text{SO}_4^- \quad (1) \]
\[ \rightarrow \beta - \alpha \text{Galp} (1) \]

Forms stiff, brittle, thermoreversible gels with $K^+ > Ca^{2+}$; thickeners and gels in milk at low concentration; synergetic gelation with LBG.

Lambda types:

\[ \rightarrow \beta - \alpha \text{Galp} 2 - \text{SO}_4^- \quad (1) \]
\[ \rightarrow \beta - \alpha \text{Galp} 2 - \text{SO}_4^- \quad (1) \]

Forms soft, resilient, thermoreversible gels with $Ca^{2+} > K^+$; gels do not synergise and have good freeze-thaw stability.

Iso types:

\[ \rightarrow \beta - \alpha \text{Galp} 4 - \text{SO}_4^- \quad (1) \]
\[ \rightarrow \beta - \alpha \text{Galp} 4 - \text{SO}_4^- \quad (1) \]

Forms soft, resilient, thermoreversible gels with $Ca^{2+} > K^+$; gels do not synergise and have good freeze-thaw stability.
<table>
<thead>
<tr>
<th>Gum</th>
<th>Source</th>
<th>Class</th>
<th>General shape</th>
<th>Monomer units and linkages (approx. ratios)</th>
<th>Noncarbohydrate substituent groups</th>
<th>Water solubility</th>
<th>Key general characteristics</th>
<th>Major food applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alginate (generally sodium alginate)</td>
<td>Brown algae</td>
<td>Seaweed extract</td>
<td>Linear</td>
<td>Block copolymer of the following units: ---4)-β-D-ManpA (1.0) ---4)-α-L-GulpA (0.5–2.5)</td>
<td>Sodium alginate soluble</td>
<td>Viscous, not very pseudoplastic solutions</td>
<td>Forms nonmelting gels (dessert gels, fruit analogs, other structured foods) Maat analogs Algic acid forms soft, thixotropic, nonmelting gels (tomato ketchup, jellied type bakery fillings, filled fruit-containing breakfast cereal products)</td>
<td></td>
</tr>
<tr>
<td>Pectins</td>
<td>Citrus peel</td>
<td>Plant extract</td>
<td>Linear</td>
<td>Primarily composed of ---4)-α-GalpA units</td>
<td>Methyl ester groups and sugars May contain amide groups</td>
<td>Soluble</td>
<td>Surface active Solutions stable to acids and Ca²⁺</td>
<td>Emulsion stabilization in creamy salad dressings Thickener in low-calorie salad dressings HMP pectin: high-sugar jellies, jams, preserves, and marmalades Acid milk drinks LM pectin: dietetic jellies, jams, preserves, and marmalades</td>
</tr>
<tr>
<td>Gum arabic (gum acacia)</td>
<td>Acacia tree</td>
<td>Exudate gum</td>
<td>Branched, highly branched</td>
<td>Complex, variable structure Contains polypeptide</td>
<td>Very high</td>
<td>Emulsifier and emulsion stabilizer Compatible with high concentrations of sugar Very low viscosity at high concentrations</td>
<td>Prevents sucrose crystallization in confections Emulsifies and distributes fatty components in confections Preparation of flavor oil-in-water emulsions Component of coating of pan-coated candies Preparation of flavor powders</td>
<td></td>
</tr>
</tbody>
</table>

*For definitions of CS and MS see Sec. 4.4.3 and 4.5.3.
4.4 Starch [32,33,38,56,61]

Starch unique chemical and physical characteristics and nutritional quality set it apart from all other carbohydrates. Starch is the predominant food reserve substance in plants and provides 70–80% of the calories consumed by humans worldwide. Starch and starch hydrolysis products constitute most of the digestible carbohydrate in the human diet. Also, the amount of starch used in the preparation of food products, without counting that present in flours used to make bread and other bakery products, that naturally occurring in grains used to make breakfast cereals, or that naturally consumed in fruits and vegetables, greatly exceeds the combined use of all other food hydrocolloids.

Commercial starches are obtained from cereal grain seeds, particularly from corn, waxy corn (waxy maize), high-amylose corn, wheat, and various rices, and from tubers and roots, particularly potato, sweet potato, and tapioca (cassava). Starches and modified starches have an enormous number of food uses, including adhesive, binding, clouding, dusting, film forming, foam strengthening, antistaling, gelling, glazing, moisture retaining stabilizing, texturizing, and thickening applications.

Starch is unique among carbohydrates because it occurs naturally as directly particules (granules). Starch granules are relatively dense ad insoluble and hydrate only slightly in cold water. They can be dispersed in water, producing low-viscosity slurries that can be easily mixed and pumped, even at concentrations of greater than 35%. The viscosity-building (thickening) power of starch is realized only when a slurry of granules is cooked. Heating a 5% slurry of unmodified starch granules to about 80°C (175°F) with stirring produces very high viscosity. A second uniqueness is that most starch granules are composed of a mixture of two polymers: an essentially linear polysaccharide called amylose, and a highly branched polysaccharide called amylopectin.

4.4.1 Amylose

While amylose is essentially a linear chain of (1 → 4)-linked D-glucopyranosyl units, many amylose molecules have a few D-(1 → 6) branches, perhaps 1 in 180–320 units, or 0.3–0.5% of the linkages [49]. The branches in branced amylose molecules are either very long or very short, and the branch points are separatd by large distances so that the physical properties of amylose molecules are essentials those of linear molecules. Amylose molecules have molecular weights of about 10^6.

The axial → equatorial position coupling of the (1 → 4)-linked D-glucopyrosy units in amylose chains gives the molecules a right-handed spiral or helical shape (Fig. 35). The interior of the helix contains only hydrogen atoms and is liophilic, while the hydroxyl groups are positioned on the exterior of the coil.

Most starches contain about 25% amylose (Table 3). The two so-called high-amylose corn starches that are commercially available have apparent amylose contents of about 52% and 70–75%.

4.4.2 Amylopectin [21,22,34]

Amylopectin is a very large, very highly branched molecule, with branch-point linkages constituting 4–5% of the total linkages. Amylopectin consists of a chain containing the only reducing end-group, called a C-chain, which has numerous branches, termed B-chains, to which one to several third-layer A-chains are attached. The branches of amylopectin mole-

*A-chains are unbranched. B-chains are branched with A-chairs or other B-chains.
Figure 35
A trisaccharide segment of an unbranched portion of an amylose or amylopectin molecule.

Molecules are clustered (Fig. 36) and occur as double helices. Molecular weights of from $10^7$ to $5 \times 10^8$ make amylopectin molecules among the largest, if not the largest, molecules found in nature.

Amylopectin is present in all starches, constituting about 75% of most common starches (Table 3.). Some starches consist entirely of amylopectin and are called waxy starches. Waxy corn (waxy maize), the first grain recognized as one in which the starch consists only of amylopectin, is so termed because when the kernel is cut the new surface appears vitreous or waxy. Other all-amylopectin starches are also called waxy although, as in corn, there is no wax content.

Potato amylopectin is unique in having phosphate ester groups, attached most often (60%-70%) at an O-6 position, with the other third at O-3 positions. These phosphate ester groups occur about once in every 215-560 $\alpha$-D-glucopyranosyl units, and about 88% of them are on B chains.

4.4.3 Starch Granules [2,21,24,37,44]

Starch granules are made up of amylose and/or amylopectin molecules arranged radially. They contain both crystalline and noncrystalline regions in alternating layers. The clustered branches of amylopectin occur as packed double helices. It is the packing together of these double-helical structures that forms the many small crystalline areas comprising the dense layers of starch granules that alternate with less dense amorphous layers. Because the crystallinity is produced by ordering of the amylopectin chains, waxy starch granules, that is, granules without amylose, have about the same amount of crystallinity as do normal starches. Amylose molecules occur among the amylopectin molecules, and some diffuse from partially water-swollen granules. The radial, ordered arrangement of starch molecules in a granule is evident from the polarization cross (white cross on a black background) seen in a polarizing microscope with the polarizers set 90° to each other. The center of the cross is at the hilum, the origin of growth of the granule.

Corn starch granules, even from a single source, have mixed shapes, with some being almost spherical, some angular, and some indented. (For the size, see Table 3.) Wheat starch granules are lenticular and have a bimodal or trimodal size distribution (> 14 µm, 5–14 µm, 1–5 µm).

*Starch granules are composed of layers somewhat like the layers of an onion, except that the layers cannot be peeled off.
<table>
<thead>
<tr>
<th></th>
<th>Common corn starch</th>
<th>Waxy maize starch</th>
<th>High-amylose corn starch</th>
<th>Potato starch</th>
<th>Tapioca starch</th>
<th>Wheat starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granule size (major axis, µm)</td>
<td>2–30</td>
<td>2–30</td>
<td>2–24</td>
<td>5–100</td>
<td>4–35</td>
<td>2–55</td>
</tr>
<tr>
<td>Amylose (%)</td>
<td>28</td>
<td>&lt;2</td>
<td>50–70</td>
<td>21</td>
<td>17</td>
<td>28</td>
</tr>
<tr>
<td>Gelatinization/pasting temperature (°C)</td>
<td>62–80</td>
<td>63–72</td>
<td>66–170&lt;sup&gt;b&lt;/sup&gt;</td>
<td>58–65</td>
<td>52–65</td>
<td>52–85</td>
</tr>
<tr>
<td>Relative viscosity</td>
<td>Medium</td>
<td>Medium high</td>
<td>Very low&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Very high</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Paste rheology&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Short</td>
<td>Long (cohesive)</td>
<td>Short</td>
<td>Very long</td>
<td>Long (cohesive)</td>
<td>Short</td>
</tr>
<tr>
<td>Paste clarity</td>
<td>Opaque</td>
<td>Very Slightly cloudy</td>
<td>Opaque</td>
<td>Clear</td>
<td>Clear</td>
<td>Opaque</td>
</tr>
<tr>
<td>Tendency to gel/retrograde</td>
<td>High</td>
<td>Very low</td>
<td>Very high</td>
<td>Medium to low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Lipid (%DS)</td>
<td>0.8</td>
<td>0.2</td>
<td>—</td>
<td>0.1</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>Protein (%DS)</td>
<td>0.35</td>
<td>0.25</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>Phosphorus (%DS)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.08</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Flavor</td>
<td>Cereal (slight)</td>
<td>“Clean”</td>
<td>Slight</td>
<td>Bland</td>
<td>Cereal (slight)</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>From the initial temperature of gelatinization to complete pasting.

<sup>b</sup>Under ordinary cooking conditions, where the slurry is heated to 95–100°C, high-amylose corn starch produces essentially no viscosity. Pasting does not occur until the temperature reaches 160–170°C (320–340°F).

<sup>c</sup>For a description of long and short flow, see Section 4.3.2.
FIGURE 36
A diagrammatic representation of a portion of an amylopectin molecule.
Rice granules, on average, are the smallest of the commercial starch granules (1.5–9 µm), although the small granules of wheat starch are almost the same size. Many of the granules in tuber and root starches, such as potato and tapioca starches, tend to be larger than those of seed starches and are generally less dense and easier to cook. Potato starch granules may be as large as 100 µm along the major axis.

All starches retain small amounts of ash, lipid, and protein (Table 3). The phosphorus content of potato starch (0.06–0.1%) is due to the presence of the phosphate ester groups on amylopectin molecules. The phosphate ester groups give potato starch amylopectin a slight negative charge, resulting in some coulombic repulsion that may contribute to the rapid swelling of potato starch granules in warm water and to several properties of potato starch pastes, namely, their high viscosities, good clarity (Table 3), and low rate of retrogradation (see Sec. 4.4.6). Cereal starch molecules either do not have phosphate ester groups or have very much smaller amounts than occurs in potato starch. Only the cereal starches contain endogenous lipids in the granules. These internal lipids are primarily free fatty acids (FFA) and lysophospholipid (LPL), largely lysophosphatidyl choline (89% in corn starch), with the ratio of FFA to LPL varying from one cereal starch to another.

4.4.4 Granule Gelatinization and Pasting

Undamaged starch granules are insoluble in cold water, but can imbibe water reversibly; that is, they can swell slightly, and then return to their original size on drying. When heated in water, starch granules undergo a process called gelatinization. Gelatinization is the disruption of molecular order within granules. Evidence for the loss of order includes irreversible granule swelling, loss of birefringence, and loss of crystallinity. Leaching of amylose occurs during gelatinization, but some leaching of amylose can also occur prior to gelatinization. Total gelatinization usually occurs over a temperature range (Table 3), with larger granules generally gelatinizing first. The apparent temperature of initial gelatinization and the range over which gelatinization occurs depend on the method of measurement and on the starch:water ratio, granule type, and heterogeneities within the granule population under observation. Several stages of gelatinization can be determined using a polarizing microscope equipped with a hot stage. These are the initiation temperature (first observed loss in birefringence), the midpoint temperature, the completion or birefringence endpoint temperature (BEPT, the temperature at which the last granule in the field under observation loses its birefringence), and the gelatinization temperature range.

Continued heating of starch granules in excess water results in further granule swelling, additional leaching of soluble components (primarily amylose), and eventually, especially with the application of shear forces, total disruption of granules. This phenomenon results in the formation of a starch paste. (In starch technology, what is called a paste is what results from heating a starch slurry.) Granule swelling and disruption produce a viscous mass (the paste) consisting of a continuous phase of solubilized amylose and/or amylopectin and a discontinuous phase of granule remnants (granule ghosts* and fragments). Complete molecular dispersion is not accomplished except, perhaps, under conditions of high temperature, high shear, and excess water, conditions seldom, if ever, encountered in the preparation of food products. Cooling of a hot corn-starch paste results in a viscoelastic, firm, rigid gel.

Because gelatinization of starch is an endothermic process, differential scanning calorimetry (DSC), which measures both the temperature and the enthalpies of gelatinization, is

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*The granule ghost is the remnant remaining after cooking under no to moderate shear. It consists of the outer portion of the granule. It appears as an insoluble, outer envelope, but is not a membrane.
widely used. Although there is not complete agreement on the interpretation of DSC data and the events that take place during gelatinization of starch granules, the following general picture is widely accepted. Water acts as a plasticizer. Its mobility-enhancing effect is first realized in the amorphous regions, which physically have the nature of a glass. When starch granules are heated in the presence of sufficient water (at least 60%), and a specific temperature (\(T_g\), the glass transition temperature) is reached, the plasticized amorphous regions of the granule undergo a phase transition from a glassy state to a rubbery state. However, the peak for absorption of energy associated with this transition is not often seen by DSC because the regions of crystallinity, that is, the ordered, packed, double-helical branches of amylopectin, are contiguous and connected by covalent bonds to the amorphous regions and melting of the crystallites immediately follows the glass transition. Because the enthalpy of initial melting (\(T_m\)) is so much larger than that of the glass transition, the latter is usually not evident.

Melting of lipid-amylose complexes occurs at much higher temperatures (100–120°C in excess water) than does melting of the amylopectin double-helical branches packed in crystalline order. These complexes are made with single-helical segments of amylose molecules when a starch paste containing monoacyl lipids is cooled. A DSC peak for this event is absent in waxy starches (without amylose).

Under normal food processing conditions (heat and moisture, although many food systems contain limited water as far as starch cooking is concerned), starch granules quickly swell beyond the reversible point. Water molecules enter between chains, break interchain bonds, and establish hydration layers around the separated molecules. This plasticizes (lubricates) chains so they become more fully separated and solvated. Entrance of large amounts of water causes granules to swell to several times their original size. When a 5% starch suspension is gently stirred and heated, granules imbibe water until much of the water is absorbed by them, forcing them to swell, press against each other, and fill the container with a highly viscous starch paste. Such highly swollen granules are easily broken and disintegrated by stirring, resulting in a decrease in viscosity. As starch granules swell, hydrated amylose molecules diffuse through the mass to the external phase (water), a phenomenon responsible for some aspects of paste behavior. Results of starch swelling can be recorded using a Brabender Visco/amylograph, which records the viscosity continuously as the temperature is increased, held constant for a time, and then decreased (Fig. 37).

By the time peak viscosity is reached, some granules have been broken by stirring. With continued stirring, more granules rupture and fragment, causing a further decrease in viscosity. On cooling, some starch molecules partially reassociate to form a precipitate or gel. This process is called retrogradation (see Sec. 4.4.6). The firmness of the gel depends on the extent of junction zone formation (see Sec. 4.3.3). Junction zone formation is influenced (either facilitated or hindered) by the presence of other ingredients such as fats, proteins, sugars, and acids and the amount of water present.

### 4.4.5 Uses of Unmodified Starches

Starches serve a variety of roles in food production. Principally they are used to take up water and to produce viscous fluids/pastes and gels and to give desired textural qualities (see also Sec. 4.4.9). The extent of starch gelatinization in baked goods strongly affects product properties, including storage behavior and rate of digestion. In some baked products, many starch granules remain ungelatinized. In certain cookies and pie crust that are high in fat and low in

\*A glass is a mechanical solid capable of supporting its own weight against flow. A rubber is an undercooled liquid that can exhibit viscous flow. (See Chap. 2 for further details.)
water, about 90% of the wheat starch granules remain ungelatinized (as observed microscopically and as evidenced by their slow rate of attack by amylases). In other products, such as angel food cake and white bread, which are higher in moisture, about 96% of the wheat starch granules are gelatinized and many become deformed.

Food companies value the clear, cohesive pastes produced from waxy maize starch. Potato starch is used in extruded cereal and snack food products and in dry mixes for soups and cakes. Rice starch produces opaque gels useful for baby food. Waxy rice starch gels are clear and cohesive. Wheat starch gels are weak; their slight flavor may be due to residual flour components. Tuber (potato) and root (tapioca) starches have weak intermolecular bonding and swell greatly to give high-viscosity pastes. Because the highly swollen granules break easily, the viscosity quickly decreases with only moderate shear. Starches are often modified (see Sec. 4.4.9) before use in foods.
4.4.6 Retrogradation and Staling [36,37,44]

As already pointed out, cooling a hot starch paste generally produces a viscoelastic, firm, rigid gel. The formation of the junction zones of a gel can be considered to be the first stage of an attempt by starch molecules to crystallize. As starch pastes are cooled and stored, the starch becomes progressively less soluble. In dilute solution, starch molecules will precipitate, with the insoluble material being difficult to redisolve by heating. The collective processes of dissolved starch becoming less soluble are called retrogradation. Retrogradation of cooked starch involves both the two constituent polymers, amylose and amylopectin, with amylose undergoing retrogradation at a much more rapid rate than does amylopectin. The rate of retrogradation depends on several variables, including the molecular ratio of amylose to amylopectin; structures of the amylose and amylopectin molecules, which are determined by the botanical source of the starch; temperature; starch concentration; and presence and concentration of other ingredients, such as surfactants and salts. Many quality defects in food products, such as bread staling and loss of viscosity and precipitation in soups and sauces, are due, at least in part, to starch retrogradation.

Staling of baked goods is noted by an increase in crumb firmness and a loss in product freshness. Staling begins as soon as baking is complete and the product begins to cool. The rate of staling is dependent on the product formulation, the baking process, and storage conditions. Staling is due, at least in part, to the gradual transition of amorphous starch to a partially crystalline, retrograded state. In baked goods, where there is just enough moisture to gelatinize starch granules (while retaining a granule identity), amylose retrogradation (insolubilization) may be largely complete by the time the product has cooled to room temperature. Retrogradation of amylopectin is believed to involve primarily association of its outer branches and requires a much longer time than amylose retrogradation, giving it prominence in the staling process that occurs with time after the product has cooled.

Most polar lipids with surfactant properties retard crumb firming. Compounds such as glyceryl monopalmitate (GMP), other monoglycerides and their derivatives, and sodium stearoyl 2-lactylate (SSL) are incorporated into doughs of bread and other baked goods, in part to increase shelf life.

4.4.7 Starch Complexes [3]

Amylose chains are helical with hydrophobic (lipophilic) interiors and are able to form complexes with linear hydrophobic portions of molecules that can fit in the hydrophobic tube. Iodine (as $I_3^-$) complexes with both amylose and amylopectin molecules. Again, the complexing occurs within the hydrophobic interior of helical segments. With amylose, the long helical segments allow long chains of poly($I_3^-$) to form and produce the blue color used as a diagnostic test for starch. The amylose-iodine complex contains 19% iodine, and determination of the amount of complexing is used to measure the amount of apparent amylose present in a starch. Amylopectin is colored a reddish-purple by iodine because the branches of amylopectin are too short for formation of long chains of poly($I_3^-$).

Polar lipids (surfactants/emulsifiers and fatty acids) can affect starch pastes and starch-based foods in one or more of three ways as a result of complex formation: (a) by affecting the processes associated with starch gelatinization and pasting (that is, the loss of birefringence, granular swelling, leaching of amylose, melting of the crystalline regions of starch granules, and viscosity increases during cooking), (b) by modifying the rheological behavior of the resulting pastes, and (c) by inhibiting the crystallization of starch molecules associated with the retrogradation process. The specific changes observed upon addition of lipid depend on its structure, the starch employed, and the product to which it is added.
4.4.8 Hydrolysis of Starch [43,48,52]

Starch molecules, like all other polysaccharide molecules, are depolymerized by hot acids. Hydrolysis of the glycosidic bonds occurs more or less randomly to produce, initially, very large fragments. Commercially, hydrochloric acid is sprayed onto well-mixed starch, or stirred moist starch is treated with hydrogen chloride gas; the mixture is then heated until the desired degree of depolymerization is obtained. The acid is then neutralized, and the product is recovered, washed, and dried. The products are still granular, but break up (cook out) easily. They are called acid-modified or thin-boiling starches, and the process of making them is called thinning. Even though only a few glycosidic bonds are hydrolyzed, the starch granules disintegrate much more easily during heating in water. Acid-modified starches form gels with improved clarity and increased strength, even though they provide less solution viscosity. Thin-boiling starches are used as film formers and adhesives in products such as pan-coated nuts and candies and whenever a strong gel is desired, such as in gum candies like jelly beans, jujubes, orange slices, and spearmint leaves and in processed cheese loaves. To prepare especially strong and fast-setting gels, a high-amylose corn starch is used as the base starch.

More extensive modification with acid produces dextrins. Low-viscosity dextrins can be used at high concentrations in food processing. They have film-forming and adhesive properties and are used in products such as pan-coated roasted nuts and candy. They are also used as fillers, encapsulating agents, and carriers of flavors, especially spray-dried flavors. They are classified by their cold water solubility and color. Dextrins that retain large amounts of linear chains or long chain fragments form strong gels.

Hydrolysis of starch dispersions with either an acid or an enzyme produces first maltodextrins. Maltodextrins are usually described by their dextrose equivalency (DE). The DE is related to the degree of polymerization (DP) through the following equation: \( \text{DE} = \frac{100}{\text{DP}} \). (Both DE and DP are average values for populations of molecules.) Therefore, the DE of a product of hydrolysis is its reducing power as a percentage of the reducing power of pure dextrose (\( \beta \)-glucose); thus, DE is inversely related to average molecular weight. Maltodextrins are defined as products with DE values that are measurable, but less than 20. Maltodextrins of lowest DE are nonhygroscopic, while those of highest DE (that is, lowest average molecule weight) tend to absorb moisture. Maltodextrins are bland with virtually no sweetness and are excellent for contributing body or bulk to food systems. Hydrolysis to DE values of 20–60 gives mixtures of molecules that, when dried, are called corn syrup solids. Corn syrup solids dissolve rapidly and are mildly sweet. Table 4 lists functional properties of starch hydrolysis products.

Continued hydrolysis of starch produces a mixture of \( \beta \)-glucose, maltose, and other

<table>
<thead>
<tr>
<th>Properties enhanced by greater hydrolysis</th>
<th>Properties enhanced in products of less conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweetness</td>
<td>Viscosity production</td>
</tr>
<tr>
<td>Hygroscopicity and humectancy</td>
<td>Body formation</td>
</tr>
<tr>
<td>Freezing point depression</td>
<td>Foam stabilization</td>
</tr>
<tr>
<td>Flavor enhancement</td>
<td>Sugar crystallization prevention</td>
</tr>
<tr>
<td>Fermentability</td>
<td>Ice crystal growth prevention</td>
</tr>
<tr>
<td>Browning reaction</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)High-conversion (high-DE) syrups.

\(^b\)Low-DE syrups and maltodextrins.
malto-oligosaccharides. Syrups of this composition are produced in enormous quantities. One of the most common has a DE of 42. These syrups are stable because crystallization does not occur easily in such complex mixtures. They are sold in concentrations of high osmolality, high enough that ordinary organisms cannot grow in them. An example is waffle and pancake syrup, which is colored with caramel coloring and flavored with maple flavoring.

Three to four enzymes are used for the industrial hydrolysis of starch to D-glucose. α-Amylase is an endo-enzyme that cleaves both amylose and amylpectin molecules internally, producing oligosaccharides. The larger oligosaccharides may be singly, doubly, or triply branched via (1 → 6) linkages, since α-amylase acts only on the (1 → 4) linkages of starch. α-Amylase does not attack double-helical starch polymer segments or polymer segments complexed with a polar lipid (stabilized single helical segments).

Glucoamylase (amyloglucosidase) is used commercially, in combination with an α-amylase, for producing D-glucose (dextrose) syrups and crystalline D-glucose. The enzyme acts upon fully gelatinized starch as an exo-enzyme, sequentially releasing single D-glucosyl units from the nonreducing ends of amylose and amylpectin molecules, even those joined through (1 → 6) bonds. Consequently, the enzyme can completely hydrolyze starch to D-glucose, but is used on starch that has been previously depolymerized with α-amylase to generate small fragments and more nonreducing ends.

- Amylase releases the disaccharide maltose sequentially from the nonreducing end of amylase. It also attacks the nonreducing ends of amylpectin, sequentially releasing maltose, but it cannot cleave the (1 → 6) linkages at branch points, so leaves a pruned amylpectin residue termed a limit dextrin, specifically a beta-limit dextrin.

There are several debranching enzymes that specifically catalyze hydrolysis of (1 → 6)-linkages in amylpectin, producing numerous linear but low-molecular-weight molecules. One such enzyme is isoamylase; another is pullulanase.

Cyclodextrin glucanotransferase is a unique Bacillus enzyme that forms rings of (1 → 4)-linked D-glucopyranosyl units from starch polymers. The enzyme can form six-, seven-, and eight-membered rings, which are respectively alpha-, beta-, and gamma-cyclodextrins. Since the normal helical conformation of a linear portion of a starch molecule contains six to seven glucosyl units per turn of the helix, this transfer of a glycosidic bond from one that joins adjacent segments of a spiral to one that forms a doughnut-like circular structure is easy to picture. These products, originally called Schardinger dextrins after their discoverer, are now known as cyclodextrins or cycloamyloses. They have the ability to complex with hydrophobic substances that are held in the center of the ring. Through such complexing of guest molecules, volatile essential oils can be converted into dry powders in which the flavoring or aromatic substance is protected from light and oxygen but is readily released when the complex is added to an aqueous system because of the water solubility of the cyclodextrin. Cyclodextrins are not yet approved for food use in the United States. However, chiral supports that are useful for chromatographic separations are made by converting cyclodextrins into insoluble polymeric materials. In a similar application, insoluble polymeric beads of cyclodextrins have been shown to be useful for removal of bitter components of citrus juices.

Corn syrup is the major source of D-glucose and D-fructose. To make a corn syrup, a slurry of starch in water is mixed with a thermally stable α-amylase and put through a cooker where rapid gelatinization and enzyme-catalyzed hydrolysis (liquefaction) takes place. After cooling to 55–60°C (130–140°F), hydrolysis is continued with glucoamylase, whereupon the syrup is clarified, concentrated, carbon-refined, and ion-exchanged. If the syrup is properly refined and combined with seed crystals, crystalline D-glucose (dextrose) or its monohydrate can be obtained.

For production of D-fructose, a solution of D-glucose is passed through a column con-
taining bound (immobilized) glucose isomerase. The enzyme catalyzes the isomerization of D-glucose to D-fructose (see Fig. 5) to an equilibrium mixture of approximately 58% D-glucose and 42% D-fructose. Higher concentrations of D-fructose are usually desired. [The high-fructose corn syrup (HFCS) most often used as a soft drink sweetener is approximately 55% D-fructose.] So the isomerized syrup is passed through a bed of cation-exchange resin in the calcium salt form. The resin binds D-fructose, which can be recovered to provide an enriched syrup fraction.

4.4.9 Modified Food Starch [1,56,58]

Food processors generally prefer starches with better behavioral characteristics than provided by native starches. Native starches produce particularly weak-bodied, cohesive, rubbery pastes when cooked and undesirable gels when the pastes are cooled. The properties of starches can be improved by modification. Modification is done so that resultant pastes can withstand the conditions of heat, shear, and acid associated with particular processing conditions and to introduce specific functionalities. Modified food starches are functional, useful, and abundant food macroingredients and additives.

Types of modifications that are most often made, sometimes singly, but often in combinations, are crosslinking of polymer chains, non-crosslinking derivatization, depolymerization (see Sec. 4.4.8), and pregelatinization (see Sec. 4.4.10). Specific property improvements that can be obtained by proper combinations of modifications are reduction in the energy required to cook (improved gelatinization and pasting), modification of cooking characteristics, increased solubility, either increased or decreased paste viscosity, increased freeze-thaw stability of pastes, enhancement of paste clarity, increased paste sheen, inhibition of gel formation, enhancement of gel formation and gel strength, reduction of gel syneresis, improvement of interaction with other substances, improvement in stabilizing properties, enhancement of film formation, improvement in water resistance of films, reduction in paste cohesiveness, and improvement of stability to acid, heat, and shear.

Starch, like all carbohydrates, can undergo reactions at its various hydroxyl groups. In modified food starches, only a very few of the hydroxyl groups are modified. Normally ester or ether groups are attached at very low DS values (degrees of substitution). DS values are usually <0.1 and generally in the range 0.002–0.2. Thus, there is, on average, one substituent group on every 500-5 D-glucopyranosyl units. Small levels of derivatization change the properties of starches dramatically and greatly extend their usefulness. Starch products that are esterified or etherified with monofunctional reagents resist interchain associations. Derivatization of starches with monofunctional reagents reduces intermolecular associations, the tendency of the starch paste to gel, and the tendency for precipitation to occur. Hence this modification is often called stabilization, and the products are called stabilized starches. Use of difunctional reagents produces crosslinked starches. Modified food starches are often both cross-linked and stabilized.

Chemical reactions currently both allowed and used to produce modified food starches in the United States are as follows: esterification with acetic anhydride, succinic anhydride, the mixed anhydride of acetic and adipic acids, 1-octenylsuccinic anhydride, phosphoryl chloride, sodium trimetaphosphate, sodium tripolyphosphate, and monosodium orthophosphate; etherification with propylene oxide; acid modification with hydrochloric and sulfuric acids; bleaching

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*The degree of substitution (DS) is defined as the average number of esterified or etherified hydroxyl groups per monosaccharide unit. Both branched and unbranched polysaccharides composed of hexopyranosyl units have an average of three hydroxyl groups per monomeric unit. Therefore, the maximum DS for a polysaccharide is 3.0.
with hydrogen peroxide, peracetic acid, potassium permanganate, and sodium hypochlorite; oxidation with sodium hypochlorite; and various combinations of these reactions.

Modified waxy maize starches are especially popular in the U.S. food industry. Pastes of unmodified common corn starch will gel, and the gels will generally be cohesive, rubbery, long textured, and prone to syneresis (that is, to weep or exude moisture). However, pastes of waxy maize starch show little tendency to gel at room temperature, which is why waxy maize starch is generally preferred as the base starch for food starches. But pastes of waxy maize starch will become cloudy and chunky and exhibit syneresis when stored under refrigerator or freezing conditions, so even waxy maize starch is usually modified to increase the stability of its pastes. The most common and useful derivatives employed for starch stabilization are the hydroxypropyl ether, the monostarch phosphate ester, and the acetate ester.

Acetylation of starch to the maximum allowed in foods (DS 0.09) lowers the gelatinization temperature, improves paste clarity, and provides stability to retrogradation and freeze-thaw stability (but not as well as hydroxypropylation). Starch phosphate monoesters (Fig. 38) made by drying starch in the presence of sodium tripolyphosphate or monosodium orthophosphate can be used to make pastes that are clear and stable, have emulsifying properties, and have freeze-thaw stability. Monostarch phosphates have a long, cohesive texture. Paste viscosity is generally high and can be controlled by varying the concentration of reagent, time of reaction, temperature, and pH. Phosphate esterification lowers the gelatinization temperature. In the United States, the maximum allowable DS with phosphate groups is 0.002.

Preparation of an alkenylsuccinate ester of starch attaches a hydrocarbon chain to its polymer molecules (Fig. 39). Even at very low degrees of substitution, starch 1-octenylsuccinate molecules concentrate at the interface of an oil-in-water emulsion because of the hydrophobicity of the alkenyl group. This characteristic makes them useful as emulsion stabilizers. Starch 1-octenylsuccinate products can be used in a variety of food applications where emulsion
stability is needed, such as in flavored beverages. The presence of the aliphatic chain tends to give the starch derivative a sensory perception of fattiness, so it is possible to use the derivatives as a partial replacement for fat in certain foods.

Hydroxypropylstarch (starch-O-CH$_2$-CHOH-CH$_3$), prepared by reacting starch with propylene oxide to produce a low level of etherification (DS 0.02–0.2, 0.2 being the maximum allowed) is a product with properties similar to those of starch acetate because it similarly has “bumps” along the starch polymer chains—that is, it is a stabilized starch. Hydroxypropylation reduces the gelatinization temperature. Hydroxypropylstarches form clear pastes that do not retrograde and withstand freezing and thawing. They are used as thickeners and extenders. To improve viscosity, particularly under acidic conditions, acetylated and hydroxypropylated starches are often also crosslinked with phosphate groups.

The majority of modified food starch is crosslinked. Crosslinking occurs when starch granules are reacted with difunctional reagents that react with hydroxyl groups on two different molecules within the granule. Crosslinking is accomplished most often by producing distarch phosphate esters. Starch is reacted with either phosphoryl chloride, PO$_2$Cl$_2$, or sodium trimetaphosphate in an alkaline slurry, then dried. Linking together of starch chains with phosphate diester or other crosslinks reinforces the granule and reduces both the rate and the degree of granule swelling and subsequent disintegration. Thus, granules exhibit reduced sensitivity to processing conditions (high temperature; extended cooking times; low pH; high shear during mixing, milling, homogenization, and/or pumping). Cooked pastes of crosslinked starches are more viscous, "heavier bodied, shorter textured, and less likely to break down during extended cooking or during exposure to low pH and/or severe agitation than are pastes of native starches from which they are prepared. Only a small amount of crosslinking is required to produce a noticeable effect; with lower levels of crosslinking, granules exhibit hydration swelling in inverse proportion to DS. As crosslinking is increased, the granules become more and more tolerant to physical conditions and acidity, but less and less dispersible by cooking. Energy requirements to reach maximum swelling and viscosity are also increased. For example, treatment of a starch with only 0.0025% of sodium trimetaphosphate greatly reduces both the rate and the degree of granule swelling, greatly increases paste stability, and changes dramatically the Brabender Visco/amylograph viscosity profile and textural characteristics of its paste. Treatment with 0.08% of trimetaphosphate produces a product in which granule swelling is restricted to the point that a peak viscosity is never reached during the hot holding period in a Brabender Visco/amylograph. As the degree of crosslinking increases, the starch also becomes more acid stable. Though hydrolysis of glycosidic bonds occurs during heating in aqueous acid, chains tied to each other through phosphate crosslinks continue to provide large molecules and an elevated viscosity. The only other crosslink permitted in a food starch is the distarch ester of adipic acid.

Most crosslinked food starches contain less than one crosslink per 1000 d-glucopyranosyl units. Trends toward continuous cooking require increased shear resistance and stability to hot surfaces. Storage-stable thickening is also provided by crosslinked starches. In retort sterilization of canned foods, crosslinked starches, because of their reduced rate of gelatinization and swelling, maintain a low initial viscosity long enough to facilitate the rapid heat transfer and temperature rise that is needed to provide uniform sterilization before granule swelling brings about the ultimately desired viscosity, texture, and suspending characteristics. Crosslinked

*Note in Figure 37 that maximum viscosity is reached when the system contains highly swollen granules. Crosslinked granules hold together. Thus, there is minimal loss of viscosity after the peak is reached.
starches are used in canned soups, gravies, and puddings and in batter mixes. Crosslinking of waxy maize starch gives the clear paste sufficient rigidity so that, when used in pie fillings, cut sections of pie hold their shape.

Starches that are both crosslinked and stabilized are used in canned, frozen, baked, and dry foods. In baby foods and fruit and pie fillings in cans and jars, they provide long shelf life. They also allow frozen fruit pies, pot pies, and gravies to remain stable under long-term storage.

Modified food starches are tailor-made for specific applications. Properties that can be controlled by combinations of crosslinking, stabilization, and thinning of corn, waxy maize, potato, and other starches include, but are not limited to, the following: adhesion, clarity of solutions/pastes, color, emulsion stabilization ability, film-forming ability, flavor release, hydration rate, moisture holding capacity, stability to acids, stability to heat and cold, stability to shear, temperature required to cook, and viscosity (hot paste and cold paste). Some characteristics imparted to the food product include, but are not limited to, the following: mouth feel, reduction of oil migration, texture, sheen, stability, and tackiness.

4.4.10 Cold-Water-Soluble (Pregelatinized) Starch

Once starch has been pasted and dried without excessive retrogradation, it can be redissolved in cold water. The largest commercial quantity of such starch is made by flowing a starch-water slurry into the nip between two nearly touching and counterrotating, steam-heated rolls. The starch slurry is gelatinized and pasted almost instantaneously, and the paste coats the rolls where it dries quickly. The dry film is scraped from the roll and ground. The resulting products, known as pregelatinized starches or instant starches, are precooked starches. They are also prepared using extruders.

Both chemically modified and unmodified starches can be used to make pregelatinized starches. If chemically modified starches are used, properties introduced by the modification(s) carry through to the pregelatinized products; thus, paste properties such as stability to freeze-thaw cycling can also be characteristics of pregelatinized starches. Pregelatinized, slightly crosslinked starch is useful in instant soup, pizza topping, and extruded snacks and in breakfast cereals.

Pregelatinized starches can be used without cooking. Finely ground pregelatinized starch forms small gel particles like a water-soluble gum, but when properly dissolved gives solutions of high viscosity. Coarsely ground products “dissolve” much more readily and produce dispersions of lower viscosity and with graininess or pulpiness that is desirable in some products. Many pregelatinized starches are used in dry mixes such as instant pudding mixes; they disperse readily with high-shear stirring or when mixed with sugar or other dry ingredients.

4.4.11 Cold-Water-Swelling Starch

Granular starch that swells extensively in cold water is made by heating common corn starch in 75–90% ethanol or by a special spray-drying process. The product is dispersible in sugar solutions or corn syrups by rapid stirring; the resulting dispersion can be poured into molds, where it sets to a rigid gel that can be sliced easily. The result is a gum candy. Cold-water-swelling starch is also useful in making desserts and in muffin batters containing particles, such as blueberries, that otherwise would settle to the bottom before the batter is thickened by heating during baking.
4.5 Cellulose: Modifications and Derivatives [60]

Cellulose is the most abundant organic compound, and therefore the most abundant carbohydrate, on earth because it is the principal cell-wall component of higher plants. (It can be argued that \(\beta\)-glucose is the most abundant carbohydrate and organic compound if we consider cellulose as a combined form of this monomeric building block.) Cellulose is a high-molecular-weight, linear, insoluble homopolymer of repeating \(\beta\)-\(\text{D}\)-glucopyranosyl units joined by (1\(\rightarrow\)4) glycosidic linkages (Fig. 40). Because of their linearity and stereoregular nature, cellulose molecules associate over extended regions, forming polycrystalline, fibrous bundles. Crystalline regions are held together by large numbers of hydrogen bonds. They are separated by, and connected to, amorphous regions. Cellulose is insoluble because, in order for it to dissolve, most of these hydrogen bonds would have to be released at once. Cellulose can, however, through substitution, be converted into water-soluble gums.

Cellulose and its modified forms serve as dietary fiber because they do not contribute significant nourishment or calories as they pass through the human digestive system. Dietary fiber does, however, serve important functions (see Sec. 4.12).

A purified cellulose powder is available as a food ingredient. High-quality cellulose can be obtained from wood through pulping and subsequent purification. Chemical purity is not required for food use because cellulosic cell-wall materials are components of all fruits and vegetables and many of their products. The powdered cellulose used in foods has negligible flavor, color, and microbial contamination. Powdered cellulose is most often added to bread to provide noncaloric bulk. Reduced-calorie baked goods made with powdered cellulose, not only have an increased content of dietary fiber, but also stay moist and fresh longer.

4.5.1 Microcrystalline Cellulose [51]

A purified, insoluble cellulose termed microcrystalline cellulose (MCC) is useful in the food industry. It is made by hydrolysis of purified wood pulp, followed by separation of the constituent microcrystals of cellulose. Cellulose molecules are fairly rigid, completely linear chains of about 3000 \(\beta\)-glucopyranosyl units and associate easily in long junction zones. However, the long and unwieldy chains do not align over their entire lengths. The end of the crystalline region is simply the divergence of cellulose chains away from order into a more random arrangement. When purified wood pulp is hydrolyzed with acid, the acid penetrates the lower density, amorphous regions, effects hydrolytic cleavage of chains in these regions, and releases individual, fringed crystallites. The released crystallites grow larger because the chains that constitute the fringes now have greater freedom of motion and can order themselves.

Two types of microcrystalline cellulose are produced, both of which are stable to both heat
and acids. Powdered MCC is a spray-dried product. Spray-drying produces agglomerated aggregates of microcrystals that are porous and sponge-like. Powdered MCC is used primarily as a flavor carrier and as an anticaking agent for shredded cheese. The second type, colloidal MCC, is water dispersible and has functional properties similar to those of water-soluble gums. To make colloidal MCC, considerable mechanical energy is applied after hydrolysis to tear apart the weakened microfibrils and provide a major proportion of colloidal-sized aggregates (<0.2 µm in diameter). To prevent rebonding of the aggregates during drying, sodium carboxymethylcellulose (CMC) is added (see Sec. 4.5.2). CMC aids in redispersion and acts as a barrier to reassociation by giving the particles a stabilizing negative charge.

The major functions of colloidal MCC are to stabilize foams and emulsions, especially during high-temperature processing; to form gels with salve-like textures (MCC does not dissolve, nor does it form intermolecular junction zones; rather it forms a network of hydrated microcrystals); to stabilize pectin and starch gels to heat; to improve adhesion; to replace fat and oil, and to control ice crystal growth. MCC stabilizes emulsions and foams by adsorbing at interfaces and strengthening interfacial films. It is a common ingredient of reduced-fat ice cream and other frozen dessert products.

4.5.2 Carboxymethylcellulose [11,26]

Carboxymethylcellulose (CMC) is widely and extensively used as a food gum. Treatment of purified wood pulp with 18% sodium hydroxide solution produces alkali cellulose. When alkali cellulose is reacted with the sodium salt of chloroacetic acid, the sodium salt of the carboxymethyl ether (cellulose-O-CH\_2-CO\_2-Na\^+) is formed (Table 2). Most commercial sodium carboxymethylcellulose (CMC) products have a degree of substitution (DS) in the range 0.4–0.8. The most widely sold type for use as a food ingredient has a DS of 0.7.

Since CMC consists of long, fairly rigid molecules that bear a negative charge due to numerous ionized carboxyl groups, electrostatic repulsion causes its molecules in solution to be extended. Also, adjacent chains repel each other. Consequently, CMC solutions tend to be both highly viscous and stable. CMC is available in a wide range of viscosity types.

CMC stabilizes protein dispersions, especially near their isoelectric pH value. Thus, egg white is stabilized with CMC for co-drying or freezing, and milk products are given improved stability against casein precipitation.

4.5.3 Methylcelluloses and Hydroxypropylmethylcelluloses [16,17]

Alkali cellulose is treated with methyl chloride to introduce methyl ether groups (cellulose-O-CH\_3). Many members of this class of gums also contain hydroxypropyl ether groups (cellulose-O-CH\_2-CHOH-CH\_3). Hydroxypropylmethylcelluloses (HPMC) are made by reacting alkali cellulose with both propylene oxide and methyl chloride. The degree of substitution with methyl ether groups of commercial methylcelluloses (MC) ranges from 1.1 to 2.2. The moles of substitution (MS) values with hydroxypropyl ether groups in commercial hydroxypropylmethylcelluloses range from 0.02 to 0.3. (Both the methylcellulose and hydroxypropylmethyl-

\*The moles of substitution or molar substitution (MS) is the average number of moles of substituent attached to a glycosyl unit of a polysaccharide. Because reaction of a hydroxyl group with propylene oxide creates a new hydroxyl group with which propylene oxide can react further, poly(propylene oxide) chains, each terminated with a free hydroxyl group, can form. Thus, because more than three moles of propylene oxide can react with a single hexopyranosyl unit, MS rather than DS must be used.
Cellulose members of this gum family are generally referred to simply as methylcelluloses. Both products are cold-water soluble because the methyl and hydroxypropyl ether group protrusions along the chains prevent the intermolecular association characteristic of cellulose.

While a few added ether groups spread along the chains enhance water solubility of cellulose (by decreasing internal hydrogen bonding), they also decrease chain hydration by replacing water-binding hydroxyl groups with less polar ether groups, giving members of this family unique characteristics. The ether groups restrict solvation of the chains to the point that they are on the borderline of water solubility. Hence, when an aqueous solution is heated, the water molecules of polymer solvation dissociate from the chain and hydration is decreased sufficiently that intermolecular associations increase and gelation occurs. Reducing the temperature once again brings about solubility, so the gelation is reversible.

Because of the ether groups, the gum chains are somewhat surface active and absorb at interfaces. This helps stabilize emulsions and foams. Methylcelluloses also can be used to reduce the amount of fat in food products through two mechanisms: (a) they provide fat-like properties so that the fat content of a product can be reduced, and (b) they reduce adsorption of fat in products being fried. The gel structure produced by thermogelation provides a barrier to oil, holds moisture, and acts as a binder.

4.6 Guar and Locust Bean Gums [19,20,31]

Guar and locust bean gums are important thickening polysaccharides for both food and nonfood uses (Table 2). Guar gum produces the highest viscosity of any natural, commercial gum. Both gums are the ground endosperm of seeds. The main component of both endosperms is a galactomannan. Galactomannans consist of a main chain of \( \beta-D\)-mannopyranosyl units joined by (1→4) bonds with single-unit \( \alpha-D\)-galactopyranosyl branches attached at O-6 (Fig. 41). The specific polysaccharide component of guar gum is guaran. In guaran, about one-half of the \( D\)-mannopyranosyl main-chain units contain a \( D\)-galactopyranosyl side chain.

The galactomannan of locust bean gum (LBG, also called carob gum) has fewer branch units than does guaran and its structure is more irregular, with long stretches of about 80 underivatized \( D\)-mannosyl units alternating with sections of about 50 units in which almost every main chain unit has an \( D\)-galactopyranosyl group glycosidically connected to its O-6 position.

Because of the difference in structures, guar gum and LBG have different physical

![Figure 41](image)

A representative segment of a galactomannan molecule.
properties, even though both are composed of long, rather rigid chains that provide high solution viscosity. Because guar gum has its galactosyl units fairly evenly placed along the chain, there are few locations on the chains that are suitable for formation of junction zones. However, LBG, with its long “naked chain” sections, can form junction zones. LBG molecules can interact with bare portions of cellulose derivatives to form junctions. This produces an increase in viscosity. LBG also interacts with xanthan (see Sec. 4.7) and carrageenan (see Sec. 4.8) helices to form rigid gels.

Guar gum provides economical thickening to numerous food products. It is used frequently in combination with other food gums, such as in ice cream, where it is used in combination with carboxymethylcellulose (see Sec. 4.5.2), carrageenan (see Sec. 4.8), xanthan (see Sec. 4.7), and LBG.

Typical products in which LBG is found are the same as those for guar gum. About 85% of LBG is used in dairy and frozen dessert products. It is rarely used alone, but in combination with other gums such as CMC, carrageenan, xanthan, and guar gum. A typical use level is 0.05–0.25%.

4.7 Xanthan [25,40]

*Xanthomonas campestris*, a bacterium commonly found on leaves of plants of the cabbage family, produces a polysaccharide, termed xanthan, that is widely used as a food gum. The polysaccharide is known commercially as xanthan gum (Table 2).

Xanthan has a backbone chain identical to that of cellulose (Fig. 43; compare with Fig. 40). In the xanthan molecule, every other \(\beta-D\)-glucopyranosyl unit in the cellulose backbone has attached, at the O-3 position, a \(\beta-D\)-mannopyranosyl-(1 \(\rightarrow\) 4)-\(\beta-D\)glucuronopyranosyl-(1 \(\rightarrow\) 2)-6-O-acetyl-\(\beta-D\)-mannopyranosyl trisaccharide unit (Fig. 42).* About half of the terminal \(\beta-D\)-mannopyranosyl units have pyruvic acid attached as a 4,6-cyclic acetal. The trisaccharide side chains interact, by secondary bonding forces, with the main chain and make the molecule rather stiff. The molecular weight is probably in the order of \(2 \times 10^6\), although much larger values, presumably due to aggregation, have been reported.

Xanthan interacts with guar gum, giving a synergistic increase in solution viscosity. The interaction with LBG produces a heat-reversible gel (Fig. 42).

Xanthan is widely used as a food gum because of the following important characteristics: solubility in hot or cold water; high solution viscosity at low concentrations; no discernible change in solution viscosity in the temperature range from 0 to 100°C, which makes it unique among food gums; solubility and stability in acidic systems; excellent compatibility with salt; interaction with other gums such as LBG; ability to stabilize suspensions and emulsions; and good solution stability when exposed to freezing and thawing. The unusual and very useful properties of xanthan undoubtedly result from the structural rigidity and extended nature of its molecules, which in turn result from its linear, cellulotic backbone, which is stiffened and shielded by the anionic trisaccharide side chains.

Xanthan is ideal for stabilizing aqueous dispersions, suspensions, and emulsions. The fact that the viscosity of its solutions changes very little with temperature—that is, its solutions do not thicken upon cooling—makes it irreplaceable for thickening and stabilizing such products as pourable salad dressings and chocolate syrup, which need to pour as easily when taken from the refrigerator as they do at room temperature, and gravies, which should

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*Bacterial heteroglycans, unlike plant heteroglycans, usually have regular, repeating-unit structures.*
neither thicken appreciably as they cool nor thin too much when hot. In regular salad dressings, xanthan is at the same time a thickener and a stabilizer for both the suspension of particulate materials and the oil-in-water emulsion. It is also a thickener and suspending agent in no-oil (reduced-calorie) dressings. In both oil-containing and no-oil salad dressings, xanthan is almost always used in combination with propylene glycol alginate (PGA) (see Sec. 4.9). PGA decreases solution viscosity and pseudoplasticity. Together they give the desired pourability associated with the pseudoplastic xanthan and the creaminess sensation associated with a nonpseudoplastic solution.

Blends of xanthan and LBG and/or guar gum are excellent ice cream stabilizers. Carrageenan is added to the mix to prevent whey separation.
FIGURE 43
Structure of the pentasaccharide repeating unit of xanthan. Note the 4,6-O-pyruvylmannopyranosyl nonreducing end unit of the trisaccharide side chain. About half of the side chains are normally pyruvylated.
4.8 Carrageenans [15,50]

The carrageenans are mixtures of several related galactans having sulfate half-ester groups attached to the sugar units (Table 2). They are extracted from red seaweeds with a dilute alkaline solution; the sodium salt of a carrageenan is normally produced. Also prepared and used is an alkali-modified seaweed flour called processed Euchema seaweed (PES) or Phillippine natural grade (PNG) carrageenan. To prepare PES/PNG carrageenan, red seaweed is treated with a potassium hydroxide solution. Because the potassium salts of the types of carrageenans found in these seaweeds are insoluble, they are not extracted out. Primarily low-molecular-weight soluble components are removed from the plants during this treatment. The remaining seaweed is dried and ground to a powder. PES/PNG carrageenan is, therefore, a composite material that contains not only the molecules of carrageenan that would be extracted with dilute sodium hydroxide, but also other cell wall materials.

The term carrageenan denotes a group or family of sulfated galactans extracted from red seaweeds. Carrageenans are linear chains of D-galactopyranosyl units joined with alternating (1→3)-D- and (1→4)-D-glycosidic linkages, with most sugar units having one or two sulfate groups esterified to a hydroxyl group at carbon atoms C-2 or C-6. This gives a sulfate content ranging from 15 to 40%. Units often contain a 3,6-anhydro ring. The principal structures are termed kappa (κ), iota (ι), and lambda (λ) (Fig. 44). The disaccharide units shown in Figure 44 represent the predominant building block of each type but are not repeating unit structures. Carrageenans, as extracted, are mixtures of nonhomogeneous polysaccharides. Carrageenan products, of which there may be well more than 100 for different specific applications from a single supplier, contain different proportions of the three main behavioral types: kappa, iota, and lambda.

Carrageenan products dissolve in water to form highly viscous solutions. The viscosity is quite stable over a wide range of pH values because the sulfate half-ester groups are always ionized, even under strongly acidic conditions, giving the molecules a negative charge.

Segments of molecules of kappa- and iota-type carrageenans exist as double helices of parallel chains. In the presence of potassium or calcium ions, thermoreversible gels form upon cooling a hot solution containing such double-helical segments. Gelation can occur in water at concentrations as low as 0.5%. When kappa-type carrageenan solutions are cooled in the presence of potassium ions, a stiff, brittle gel results. Calcium ions are less effective in causing gelation. Potassium and calcium ions together produce a high gel strength. Kappa-type gels are the strongest of the carrageenan gels. These gels tend to synerese as junction zones extend within the structure. The presence of other gums retards syneresis.

Iota types are a little more soluble than are kappa-type carrageenans, but again only the sodium salt form is soluble in cold water. Iota types gel best with calcium ions. The resulting gel is soft and resilient, has good freeze-thaw stability, and does not synerese, presumably because iota-type carrageenans are more hydrophilic and form fewer junction zones than do kappa-type carrageenans.

During cooling of solutions of kappa- or iota-type carrageenans, gelation occurs because the linear molecules are unable to form continuous double helices due to the presence of structural irregularities. The linear helical portions then associate to form a rather firm three-dimensional, stable gel in the presence of the appropriate cation (Fig. 45). All salts of lambda-type carrageenans are soluble and nongelling.

Under conditions in which double helical segments occur, carrageenan molecules, particularly those of the kappa type, form junction zones with the naked segments of LBG to produce rigid, brittle, syneresing gels. This gelation occurs at a concentration one-third that needed to form a pure kappa-type carrageenan gel.
Carrageenans are most often used because of their ability to form gels with milk and water. Blending provides a wide range of products that are standardized with various amounts of sucrose, glucose (dextrose), buffer salts, or gelling aids, such as potassium chloride. The available commercial products form a variety of gels: gels that are clear or turbid, rigid or elastic, tough or tender, heat-stable or thermally reversible, and do or do not undergo syneresis. Carrageenan gels do not require refrigeration because they do not melt at room temperature. They are freeze-thaw stable.

A useful property of carrageenans is their reactivity with proteins, particularly those of milk. Kappa-type carrageenans complex with kappa-casein micelles of milk, forming a weak, thixotropic, pourable gel. The thickening effect of kappa-carrageenans in milk is 5–10 times greater than it is in water. This property is used in the preparation of chocolate milk where the thixotropic gel structure prevents settling of cocoa particles. Such stabilization requires only about 0.025% gum. This property is also utilized in the preparation of ice cream, evaporated
A representation of the hypothesized mechanism of gelation of kappa- and iota-type carrageenans. In a hot solution, the polymer molecules are in a coiled state. As the solution is cooled, they intertwine in double-helical structures. As the solution is cooled further, the double helices are believed to nest together with the aid of potassium or calcium ions.

milk, infant formulas, freeze-thaw stable whipped cream, and emulsions in which milk fat is replaced with a vegetable oil.

The synergistic effect between kappa-carrageenan and locust bean gum (LBG) (Fig. 42) produces gels with greater elasticity and gel strength, and less syneresis than gels of potassium kappa-carrageenan alone. As compared to kappa-type carrageenan alone, the kappa-type carrageenan-LBG combination provides greater stabilization and air bubble retention (overrun) in ice cream, but also a little too much chewiness, so guar gum is added to soften the gel structure.

Cold hams and poultry rolls take up 20–80% more brine when they contain 1–2% of a kappa-type carrageenan. Improved slicing also results. Carrageenan coatings on meats can serve as a mechanical protection and a carrier for seasonings and flavors. Carrageenan is sometimes added to meat analogs made from casein and vegetable proteins. A growing use of carrageenan is to hold water and maintain water content, and therefore softness of meat products, such as wiener and sausages, during the cooking operation. Addition of a kappa- or iota-type carrageenan in the Na+ form or PES/PNG carrageenan to low-fat ground beef improves texture and
hamburger quality. Normally, fat serves the purpose of maintaining softness, but because of the binding power of carrageenan for protein and its high affinity for water, carrageenans can be used to replace in part this function of natural animal fat in lean products.

Two other food gums, agar and furcellaran (also called Danish agar), also come from red seaweeds and have structures and properties that are closely related to those of the carrageenans.

4.9 Algins [5,28]

Commercial algin is a salt, most often the sodium salt, of a linear poly (uronic acid), alginic acid, obtained from brown seaweeds (Table 2). Alginic acid is composed of two monomeric units, \(-\text{D}-\text{mannopyranosyluronic acid}\) and \(-\text{L}-\text{gulopyranosyluronic acid}\) units. These two monomers occur in homogeneous regions (composed exclusively of one unit or the other) and in regions of mixed units. Segments containing only \(-\text{D}-\text{mannuronopyranosyl}\) units are referred to as M blocks and those containing only \(-\text{L}-\text{guluronopyranosyl}\) units as G blocks. \(-\text{D}-\text{Mannuronopyranosyl}\) units are in the \(4C_1\) conformation, while \(-\text{L}-\text{guluronopyranosyl}\) units are in the \(1C_4\) conformation (see Sec. 4.1.2 and Fig. 46), which gives the different blocks quite different chain conformations. M-Block regions are flat and ribbon-like, similar to the conformation of cellulose (see Sec. 4.5), because of the equatorial \(\rightarrow\) equatorial bonding. G-block regions have a pleated (corrugated) conformation as a result of its axial \(\rightarrow\) axial glycosidic bonds. Different percentages of the different block segments cause algins (alginates) from different seaweeds to have different properties. Algins with high G-block contents produce gels of high strength.

Solutions of sodium alginates are highly viscous. The calcium salt of alginates is insoluble. The insoluble salt results from the autocooperative reaction between calcium ions and the G-block regions of the chain. The holes formed between two G-block chains are cavities that bind calcium ions. The result is a junction zone that has been called an “egg box” arrangement.

![Diagram of aminopolysaccharide units](image)

**FIGURE 46**
Units of \(-\text{D}-\text{mannopyranosyluronic acid}\) (\(\text{ManpA}\)) in the \(4C_1\) conformation and \(-\text{L}-\text{gulopyranosyluronic acid}\) (\(\text{LGulpA}\)) in the \(1C_4\) conformation.
with the calcium ions being likened to eggs in the pockets of an egg carton (Fig. 47). The strength of the gel depends on the content of G blocks in the alginate used and the concentration of calcium ions.

Propylene glycol alginates are made by reacting moist alginic acid with propylene oxide to produce a partial ester with 50–85% of the carboxyl groups esterified. Solutions of propylene alginates (PGA) are much less sensitive to low pH values and polyvalent cations, including calcium ions and proteins, than are solutions of nonesterified alginates, because esterified carboxyl groups cannot ionize. Also, the propylene glycol group introduces a bump on the chain that prevents close association of chains. Therefore, PGA solutions are quite stable. Because of its tolerance to calcium ions, propylene glycol alginates can be used in dairy products. The hydrophobic propylene glycol groups also give the molecule mild interfacial activity, that is, foaming, emulsifying, and emulsion-stabilizing properties.

Algin is widely used to provide high viscosity at low concentrations. Even greater viscosity under low-shear conditions can be achieved by introducing a small amount of calcium ions. If PGA is used, some calcium ion cross-linking of chains still occurs through the remaining carboxylate groups, and results in thickening of solutions (rather than gelling).

Calcium alginate gels are obtained by diffusion setting, internal setting, and setting by cooling. Diffusion setting can be used to prepare structured foods. Perhaps the best example is the structured pimento strip. In the production of pimento strips for stuffing green olives, pimento puree is first mixed with water containing a small amount of guar gum as an immediate thickener, and then with sodium alginate. The mixture is pumped onto a conveyor belt and gelled by the addition of calcium ions. The set sheet is cut into thin strips and stuffed into olives. Internal setting for fruit mixes, purees, and fruit analogs involves slow release of calcium ions within the mixture. Setting by cooling involves dissolving a calcium salt, a slightly soluble acid, and a sequestrant in hot water and allowing the mixture to set on cooling. Gels produced in this way are quite stable. Alginate gels are reasonably heat stable and show little or no syneresis; those containing fruit can be used for fillings that remain stable through pasteurization and cooling. Unlike gelatin gels, alginate gels are not thermoreversible and can be used as dessert gels that do not require refrigeration.

Algic acid, an alginate solution whose pH has been lowered, with and without addi-
tion of some calcium ions, is employed in the preparation of soft, thixotropic, nonmelting gels (Table 2).

Propylene glycol alginate is used when stability to acid, nonreactivity with calcium ions (for example, in milk products), or its surface-active property is desired. Accordingly, it finds use as a thickener in salad dressings (Table 2). In low-calorie dressings, it is often used in conjunction with xanthan (see Sec. 4.7).

4.10 Pectins [4,41]

Commercial pectins are galacturonoglycans [poly(-D-galactopyranosyluronic acids)] with various contents of methyl ester groups (Table 2). Native pectins found in the cell walls and intercellular layers of all land plants are more complex molecules that are converted into commercial products during extraction with acid. Commercial pectin is obtained from citrus peel and apple pomace. Pectin from lemon and lime peel is the easiest to isolate and is of the highest quality. Pectins have an unique ability to form spreadable gels in the presence of sugar and acid or in the presence of calcium ions and are used almost exclusively in these types of applications.

The compositions and properties of pectins vary with source, the processes used during preparation, and subsequent treatments. During extraction with mild acid, some hydrolytic depolymerization and hydrolysis of methyl ester groups occurs. Therefore, the term pectin denotes a family of compounds, and this family is part of a still larger family called pectic substances. The term pectin is usually used in a generic sense to designate those water-soluble galacturonoglycan preparations of varying methyl ester contents and degrees of neutralization that are capable of forming gels. In all natural pectins, some of the carboxyl groups are in the methyl ester form. Depending on the isolation conditions, the remaining free carboxylic acid groups may be partly or fully neutralized, that is, partly or fully present as sodium, potassium, or ammonium carboxylate groups. Typically, they are present in the sodium salt form.

By definition, preparations in which more than half of the carboxyl groups are in the methyl ester form (-COOCH₃) are classified as high-methoxyl (HM) pectins (Fig. 48); the remainder of the carboxyl groups will be present as a mixture of free acid (-COOH) and salt (-COO⁻Na⁺) forms. Preparations in which less than half of the carboxyl groups are in the methyl ester form are called low-methoxyl (LM) pectins. The percentage of carboxyl groups esterified with methanol is the degree of esterification (DE). Treatment of a pectin preparation with ammonia dissolved in methanol converts some of the methyl ester groups into carboxamide groups (15–25%). In the process, a low-methoxyl (LM) pectin (by definition) is formed. These products are known as amidated LM pectins.

The principal and key feature of all pectin molecules is a linear chain of (1→4)-linked -D-galactopyranosyluronic acid units. Neutral sugars, primarily L-rhamnose, are also present. In citrus and apple pectins, the -L-rhamnopyranosyl units seem to be inserted into the polysaccharide chain at rather regular intervals. The inserted L-rhamnopyranosyl units may

![Figure 48](image_url)

**Figure 48**
The most prevalent monomeric unit of a high-methoxyl pectin.
provide the necessary irregularities in the structure required to limit the size of the junction zones and effect gelation. At least some pectins contain covalently attached, highly branched arabinogalactan chains and/or short side chains composed of D-xylosyl units. The presence of side chains may also be a factor that limits the extent of chain association. Junction zones are formed between regular, unbranched pectin chains when the negative charges on the carboxylete groups are removed (addition of acid), when hydration of the molecules is reduced (by addition of a cosolute, almost always sugar, to a solution of HM pectin), and/or when pectinic acid polymer chains are bridged by calcium cations.

HM pectin solutions gel when sufficient acid and sugar are present. As the pH of a pectin solution is lowered, the highly hydrated and charged carboxylete groups are converted into uncharged, only slightly hydrated carboxylic acid groups. As a result of losing some of their charge and hydration, the polymer molecules can now associate over a portion of their length, forming junctions and a network of polymer chains that entraps the aqueous solution of solute molecules. Junction zone formation is assisted by the presence of a high concentration (~65%, at least 55%) of sugar, which competes for water of hydration and reduces solvation of the chains, allowing them to interact with one another.

LM pectin solutions gel only in the presence of divalent cations, which provide crossbridges. Increasing the concentration of divalent cations (only calcium ion is used in food applications) increases the gelling temperature and gel strength. The same general egg-box model used to describe the formation of calcium alginate gels (see Sec. 4.9) is used to explain gelation of solutions of LM and amidated LM pectins upon addition of calcium ions. LM pectin, since it does not require sugar for gelation, is used to make dietetic jams, jellies, and marmalades.

4.11 Gum Arabic [14,53]

When the bark of some trees and shrubs is injured, the plants exude a sticky material that hardens to seal the wound and give protection from infection and desiccation. Such exudates are commonly found on plants that grow in semiarid climates. All require cleaning and pasteurization, since they are sticky when freshly exuded and trap dust, sand particles, insects, bacteria, and/or pieces of bark. Gum arabic (gum acacia), gum karaya, and gum ghatti are exudates of trees; gum tragacanth is the exudate of a shrub. Their overall use has diminished and continues to diminish because of their uncertain and restricted availability and their increasing cost. Only gum arabic still has a good market in its traditional food applications.

Gum arabic (gum acacia) is an exudate of acacia trees, of which there are many species distributed over tropical and subtropical regions (Table 2). The most important growing areas for species that give the best gum are the Sudan and Nigeria.

Gum arabic is a heterogeneous material, but generally consists of two fractions. One, which accounts for about 70% of the gum, is composed of polysaccharide chains with little or no nitrogenous material. The other fraction contains molecules of higher molecular weight that have protein as an integral part of their structures. The protein-polysaccharide fraction is itself heterogeneous with respect to protein content. The polysaccharide structures are covalently attached to the protein component by linkage to hydroxyproline and, perhaps, serine units, the two predominant amino acids in the polypeptide. The overall protein content is about 2 wt%, but specific fractions may contain as much as 25 wt% protein.

The polysaccharide structures, both those attached to protein and those that are not, are highly branched, acidic arabinogalactans with the following approximate composition: D-galactose, 44%; L-arabinose, 24%; D-glucuronic acid, 14.5%; L-rhamnose, 13%; 4-O-methyl-D-glucuronic acid, 1.5%. They contain main chains of (1 \rightarrow 3)-linked D-galactopyranosyl units
having two- to four-unit side chains consisting of \((1 \rightarrow 3)\)-\(\beta\)-D-galactopyranosyl units joined to it by \((1 \rightarrow 6)\)-linkages. Both the main chain and the numerous side chains have attached \(-L\)-arabinofuranosyl, \(-L\)-rhamnopyranosyl, \(-\beta\)-D-glucuronopyranosyl, and \(4-O\)-methyl-\(-\beta\)-D-glucuronopyranosyl units. The two uronic acid units occur most often as ends of chains.

Gum arabic dissolves easily when stirred in water. It is unique among the food gums because of its high solubility and the low viscosity of its solutions. Solutions of 50% concentration can be made. At this concentration, the dispersion is somewhat gel-like.

Gum arabic is both a fair emulsifying agent and a very good emulsion stabilizer for flavor oil-in-water emulsions. It is the gum of choice for emulsification of citrus, other essential oils, and limitation flavors used as baker's emulsions and concentrations for soft drinks. The soft drink industry consumes about 30% of the gum supply as an emulsifier and stabilizer. For a gum to have an emulsion-stabilizing effect, it must have anchoring groups with a strong affinity for the surface of the oil and a molecular size large enough to cover the surfaces of dispersed droplets. Gum arabic has surface activity and forms a thick, sterically stabilizing, macromolecular layer around oil droplets. Emulsions made with flavor oils and gum arabic can be spray-dried to produce dry flavor powders that are nonhygroscopic and in which the flavor oil is protected from oxidation and volatilization. Rapid dispersion and release of flavor without affecting product viscosity are other attributes. These stable flavor powders are used in dry package products such as beverage, cake, dessert, pudding, and soup mixes.

Another important characteristic is its compatibility with high concentrations of sugar. Therefore, it finds widespread use in confections with a high sugar content and a low water content. More than half the world's supply of gum arabic is used in confections such as caramels, toffees, jujubes, and pastilles. Its functions in confections are to prevent sucrose crystallization and to emulsify and distribute fatty components. Avoidance of surface accumulation of lipids is important because this occurrence results in a greasy surface whitening, called bloom. Another use is as a component of the glaze or coating of pan-coated candies.

4.12 Dietary Fiber and Carbohydrate Digestibility [7,23,29,45,46,54,57]

Dietary fiber is not necessarily fibrous in nature. Dietary fiber is a nutritional term that has nothing to do with its physical or chemical nature, although both chemical and physical properties are involved in its determination. Dietary fiber is actually defined by the method used to measure it, of which there are several. Both insoluble plant cell-wall materials, primarily cellulose and lignin, and nonstarch, water-soluble polysaccharides are components of dietary fiber. The only common feature of these substances is that they are nondigestible polymers. Therefore, not only do natural components of foods contribute dietary fiber, but so also do gums that are added to modify rheological properties, to provide bulk, and/or to provide other functionalities as already described.

One natural component of dietary fiber is a water-soluble polysaccharide, commonly known as \(-\beta\)-glucan, but more properly \(-\beta\)-\(D\)-glucan, that is present in oat and barley brans. Oat \(-\beta\)-glucan has become a commercial food ingredient because it has been shown to be effective in reducing the level of serum cholesterol. Oat \(-\beta\)-glucan is a linear chain of \(-\beta\)-D-glucopyranosyl units. About 70% are linked \((1 \rightarrow 4)\) and about 30% \((1 \rightarrow 3)\). The \((1 \rightarrow 3)\) linkages occur singly and are separated by sequences of two or three \((1 \rightarrow 4)\) linkages. Thus, the molecule is composed of \((1 \rightarrow 3)\)-linked \(-\beta\)-cellotriosyl \([\rightarrow 3](-\text{GlcP}-)\)(\(1 \rightarrow 4)\)-GlcP-\((1 \rightarrow 4)\)
Carbohydrates have always been the principal source of metabolic energy for humans and the means for maintaining health of the human gastrointestinal tract. Carbohydrates are the principal providers of the bulk and body of food products.

The higher saccharides may be digestible (most starch-based products), partially digestible (retrograded amylose, the so-called resistant starch), or nondigestible (essentially all other polysaccharides). When digestive hydrolysis to monosaccharides occurs, the products of digestion are absorbed and catabolized. [Only D-glucose is produced by digestion of polysaccharides (starch) in humans.] Those carbohydrates not digested to monosaccharides by human enzymes in the small intestine (all others except sucrose, lactose, and those related to starch) may be metabolized by microorganisms in the large intestine, producing substances that are absorbed and catabolized for energy. Therefore, carbohydrates may be caloric, partially caloric, or essentially noncaloric. They may be soluble or insoluble, and they may produce high or low viscosities. Naturally occurring plant carbohydrates are nontoxic.

The most common bulking agents in natural food are remnants of plant cells resistant to hydrolysis by enzymes in the alimentary tract. This material includes cellulose, hemicelluloses, pectin, and lignin. Dietary fiber bulking agents are important in human nutrition because they maintain normal functioning of the gastrointestinal tract. They increase intestinal and fecal bulk, which lowers intestinal transit time and helps prevent constipation. Their presence in foods induces satiety at meal time. Nutritionists set requirements of dietary fiber at 25–50 g/day. Insoluble fiber bulking agents are claimed to decrease blood cholesterol levels, lessening the chance of heart disease. They also reduce the chances of colonic cancer, probably due to their sweeping action.

Soluble gums other than β-glucans have similar effects in the gastrointestinal tract and on the level of cholesterol in blood, but to different extents. Some gums that have been specifically examined in this regard are pectin, guar gum, xanthan, and hemicelluloses. [For example, guar gum ingested at a rate of 5 g/day results in an improved glycemic index, a 13% lowering of serum cholesterol, and no decrease in the high-density lipoprotein (HDL) fraction, the beneficial cholesterol carrier.] In addition to cereal brans, kidney and navy beans are especially good sources of dietary fiber. A product based on psyllium seed hulls has high water-binding properties, leading to rapid transit time in the gastrointestinal tract, and is used to prevent constipation. A product with a methylcellulose base is sold for the same purpose.

![Figure 49](image-url)

Representative structure of a segment of oat and barley β-glucans where n usually is 1 or 2, but occasionally may be larger (shorthand notation).
The starch polysaccharides are the only polysaccharides that can be hydrolyzed by human digestive enzymes. They, of course, provide \( \alpha \)-glucose, which is absorbed by microvilli of the small intestine to supply the principal metabolic energy of humans. Other polysaccharides consumed normally as natural components of edible vegetables, fruits, and other plant materials, and those food gums added to prepared food products, are not digested in the upper digestive tract of humans, but pass into the large intestine (colon) with little or no change. (The acidity of the stomach is not strong enough, nor is the residence time of polysaccharides in the stomach sufficiently long, to cause significant chemical cleavage.) When the undigested polysaccharides reach the large intestine, they come into contact with normal intestinal microorganisms, some of which produce enzymes that catalyze hydrolysis of certain polysaccharides or certain parts of polysaccharide molecules. The consequence of this is that polysaccharides not cleaved in the upper intestinal tract may undergo cleavage and microbial metabolism within the large intestine.

Sugars that are split from the polysaccharide chain are used by the microorganisms of the large intestine as energy sources in anaerobic fermentation pathways that produce lactic, propionic, butyric, and valeric acids. These short-chain acids can be absorbed through the intestinal wall and metabolized, primarily in the liver. In addition, a small, though significant in some cases, fraction of the released sugars can be taken up by the intestinal wall and transported to the portal bloodstream where they are conveyed to the liver and metabolized. It is calculated that, on average, 7% of human energy is derived from sugars split from polysaccharides by microorganisms in the large intestine and/or from the acid by-products produced from them by these microorganisms via anaerobic fermentation. The extent of polysaccharide cleavage depends on the abundance of the particular organism(s) producing the specific enzymes required. Thus, when changes occur in the type of polysaccharide consumed, utilization of the polysaccharide by colonic microorganisms may be temporarily reduced until organisms capable of splitting the new polysaccharide proliferate.

Some polysaccharides survive almost intact during their transit through the entire gastrointestinal tract. These, plus larger segments of other polysaccharides, give bulk to the intestinal contents and lower transit time. They can be a positive factor in health through a lowering of blood cholesterol concentration, perhaps by sweeping out bile salts and reducing their chances for reabsorption from the intestine. In addition, the presence of large amounts of hydrophilic molecules maintains a water content of the intestinal contents that results in softness and consequent easier passage through the large intestine.

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