GUMS

1. Introduction

The term gum does not designate a scientific class of substances that can be defined precisely. The term is applied to a variety of substances that produce sticky or slimy, viscous solutions or molecular dispersions or gels in an appropriate solvent or swelling agent. Some are specific chemical substances. Some are materials that contain several components. As employed in industry, the term most often refers to hydrophilic, natural polymers or modifications of natural polymers that thicken or gel aqueous systems at low concentrations. More specifically, the term gum most often refers to water-soluble polysaccharides and derivatized polysaccharides. When used as ingredients in food products, polysaccharidic gums, along with certain proteins, especially gelatin, are sometimes referred to as hydrocolloids.

Polysaccharidic gums may be extracted from tissues of higher plants or marine algae; they may be exudates of trees or shrubs; they may be produced by microorganisms, or they may be water-soluble modifications of polysaccharides, such as derivatives of cellulose. Certain hydrophobic substances obtained from higher plants are also known as gums, and there are petroleum-based substances called gums. Among the latter are high molecular weight hydrocarbons and certain synthetic polymers. Nonwater-soluble gummy substances obtained from plants include the resinous saps from conifers, such as gum balsam and gum resin, incense gums, such as myrrh, huataco, and frankincense, and chicle (chewing gum). However, as mentioned above, the term gum is most often applied to certain water-soluble polysaccharides. This article covers those substances included in the most common use of the term, viz, those carbohydrate polymers (polysaccharides) of commercial importance.

With only a few exceptions, there are multiple producers and many suppliers of each gum. In many applications, especially in formulating food products, more than one gum product will provide the desired final property or properties, be compatible with other components of the system, and be compatible with the necessary processing and storage conditions. However, it is often the case that one specific type and grade of gum is superior to others. The important cost of a gum is not the cost per unit weight, but the cost of the amount of the gum product in question needed to give the desired viscosity, gel strength, or some other attribute. Gums are often used in combinations, sometimes because a synergism gives a desired property or functionality and sometimes to make use of their individual attributes. As with the individual gums, there are multiple producers and suppliers of gum blends.

Historically, the term gum was used with the exudate gums of commerce, such as gum arabic, gum karaya, gum tragacanth, and gum ghatti. These materials, which are actually mixtures of polymeric substances, were called gums long before their polysaccharidic nature was known. To most, all commercially important polysaccharides other than starch, cellulose itself, and the glycosaminoglycans, such as heparin and chondroitin sulfate, which have medical uses, should be called gums, so the gum family includes cellulose derivatives in which cellulose molecules have been modified to make them water soluble and give them properties like those of natural gums. Polysaccharides other than cellulose, especially starch and guar gum, are also chemically modified to confer on them improved properties and functionalities.

When the only gums of commerce were the exudate gums, the term gum designated those polysaccharides of plant origin containing three or more different monosaccharide units and with highly branched, complex structures. Today, polysaccharides without branch-on-branch structures are also called gums; examples are guar gum and locust bean gum (both galactomannans) and larch gum (an arabinogalactan). Commercial gums may be in their native structures or their structures may have been altered, often intentionally, but sometimes unintentionally, by the production (isolation) procedure used.

To those in the food, petroleum production, ore-refining, and many other industries that produce or use gums, the term gum is usually defined by the general feature that they are at least partially soluble in room-temperature water, forming viscous solutions, usually at low concentrations, although there are exceptions to the latter. Another commonality is that they have current or potential commercial importance, although this requirement is also stretched in some cases.

Commercial polysaccharidic gums are obtained from the seeds, roots, and tubers of land plants, from seaweeds, from microorganisms (fermentation), and by derivatization of cellulose (from farms and forests) (Table 1). Since polysaccharides are abundant, come from renewable sources, are safe (nontoxic), are amenable to both chemical and biochemical modification, and are biodegradable, it is not surprising that they find widespread and extensive use. Industrial gums are most often used because of their ability to thicken or gel aqueous systems at low concentration, but these general behaviors are manifested in a variety of ways because polysaccharides used as gums have a variety of structures. In addition, they are often also employed to impart properties other than thickening or gelation to a system.

Starches and modified starch products are not considered as gums, even though they, like the gums, are composed of water-soluble polysaccharides that can provide viscous solutions or gels at relatively low concentrations and are extensively used in practical applications.

2. General Structural Features

Polysaccharides occur in Nature in a variety of chemical and three-dimensional (3D) structures. Consequently, they comprise a family of functionally diverse biopolymers. Modification expands this diversity. Polysaccharides (glycans) are polydisperse (individual molecules differ in molecular weight) and polymolecular (individual molecules differ in fine structure) polymers of monosaccharides (sugars). The monosaccharide (glycosyl) units may be organized in linear or branched arrangements. In branched polysaccharides, other than bacterial polysaccharides, there is considerable variation in the frequency of branching, the distances between branches, and the organization of branches from molecule to molecule. Branched polysaccharide molecules span the spectrum from linear molecules decorated with short (mono-, di-, or trisaccharide) branches to branch-on-branch, bushlike structures. Some polysaccharides are neutral; some have a negative charge; only chitosan is cationic. There is also considerable variation in the amount of charge on anionic gums from molecule to molecule. The number of glycosyl units in a glycan is termed its degree of polymerization (DP) and varies widely, even within a single polysaccharide (gum) preparation. Most have average DPs of $200-3000$ (average MW of 30,000–500,000). Large molecules, like those of cellulose, have average DPs from 7,000 to 15,000 (average MW of $1.1-2.5 \times 10^6$).

Polysaccharide gums can be classified by source, solubility, the number of different glycosyl units in their structures, shape, charge, and whether or not they will form a gel. In Table 1, commercial polysaccharidic gums are classified by source.

If all the glycosyl (monomer) units of a polysaccharide are of the same sugar, the polysaccharide is a homoglycan. Examples of homoglycans are cellulose and amylose, which are linear polymers, and amylopectin, a branch-

Table 1. **Industrial Gums by Source**

Seed gums	Chemical abstracts numbers
β-glucans	[9041-22-9]
guar gum	[9000-30-0]
locust bean (carob) gum	[9000-40-2]
tara gum	[39300-88-4]
ethers of guar gum	
carboxymethylguar gums	[51190-15-3]
carboxymethylhydroxypropylguar gums	[3954-79-0]
hydroxyethylguar gums	[39465-11-7]
hydroxypropylguar gums	[39421-75-5]
2-hydroxy-3-(trimethylammonium chloride) propylguar gums	[67034-33-7, 65497-29-2]
Seaweed (algal) extracts	**Chemical Abstracts Numbers**
alginates	[9005-38-3, 9005-34-9, 9005-36-1]
modified algin	
propylene glycol alginates	[9005-34-9]
agar/agarose	[9002-18-0, 9012-36-6]
carrageenans	[1114-20-8, 9062-07-1, 9064-57-1]
furcellaran	[9000-21-9]
Plant extracts	**Chemical Abstracts Numbers**
larch gum	[37320-79-9]
pectins	[9000-69-5]
modified pectins	
low methoxyl pectins	[9049-34-7]
amidated pectins	[9000-69-5]
Fermentation (microbial) gums	**Chemical Abstracts Numbers**
curdlan	[54724-00-4]
gellans	[142804-65-7, 71010-52-1]
rhamsan	[96949-21-2]
welan	[96949-32-3]
xanthans	[11138-66-2]
Exudate gums	**Chemical Abstracts Numbers**
gum arabics	[9000-01-5]
gum tragacanth	[9000-65-1]
Tuber gum	**Chemical Abstracts Numbers**
konjac mannan	[37220-17-0]
Cellulose derivatives	**Chemical Abstracts Numbers**
carboxymethlycelluloses	[9004-42-6, 9004-32-4]
carboxymethylhydroxyethylcelluloses	[9004-30-2]
2,3-dihydroxypropylcelluloses [*O*-(1,2-propanediolcelluloses)]	[57608-21-6]
hydroxybutylmethylcelluloses	[9041-56-9, 37228-15-2]
hydroxyethylcelluloses	[9004-62-0]
hydroxyethylhydroxypropylcelluloses	[51331-09-0]
hydroxyethylmethylcelluloses	[9032-42-2]
hydroxypropylcelluloses	[9004-64-2]
hydroxypropylmethylcelluloses	[9004-65-3]
methylcelluloses	[9004-67-5]
methylethylcelluloses	[9004-59-5]
Synthetic	**Chemical Abstracts Numbers**
polydextroses	[68424-04-4]

on-branch polymer. All three polysaccharides are composed only of D-glucopyranosyl units. Even among the linear homoglycans, some consist of units all of which are connected by the same linkage type and some contain two different linkage types. Other homoglycans may consist of a main chain of units of one linkage type with mono- or disaccharide side units attached by another linkage type.

Heteroglycans are polysaccharides composed of two or more different glycosyl units. Both homoglycans and heteroglycans may contain acidic sugar units. A polysaccharide that contains two different monosaccharide units is a diheteroglycan. Diheteroglycans generally are either strictly linear, block-type copolymers (algins are an example of this type of polysaccharide) or consist of a linear chain of one type of glycosyl unit with a second present as single-unit branches. (The galactomannans, guar gum, and locust bean gum, are examples of this type of polysaccharide. Technically they are branched, but they behave as linear polymers.) Some diheteroglycans have repeating disaccharide units in a linear chain. Tri- and tetraheteroglycans are most often, but not always, branched structures, with the tetraheteroglycans usually having the most highly branched structures. Pentaheteroglycans are branch-on-branch plant polysaccharides. Individual glycosyl units of naturally occurring polysaccharides may be esterified (with acetate, glycolate, succinate, phosphate, or sulfate groups), etherified (with methyl or ethyl groups), and/or contain pyruvyl cyclic acetal groups. Naturally occurring polysaccharides may be chemically modified by a gum manufacturer or processor. Modification is used to convert an insoluble polymer (cellulose) into a water-soluble gum and to modify the functional characteristics (generally the rheological properties) of an already water-soluble polysaccharide. Most land plant and seaweed polysaccharides are not made up of regular repeating unit structures and exhibit variations in proportions of monosaccharide units, in proportions of linkage types, or in both.

3. General Properties

Solutions of polysaccharidic gums exhibit the characteristics of solutions of hydrated polymer molecules or, because intermolecular interactions are common, associations of polymer molecules. The usefulness of industrial gums is based on their physical properties. Their common characteristic is the ability to modify the flow characteristics of aqueous systems and/or to bind and hold water. The rheology (flow characteristics and gel properties) of most gum solutions is non-Newtonian. A given gum also often imparts other functional properties, and the choice of which gum to use for a particular application often depends on these other properties. Use levels of gums are usually $<2\%$ (based on the amount of water) and often $<1\%$.

Polysaccharides in Nature are heterogeneous with respect to molecular size, that is, any preparation from any source contains molecules in a range of molecular weights. Polysaccharides can be rather easily depolymerized by acid- and enzyme-catalyzed hydrolysis of the glycosidic (acetal) linkages joining the monomeric (saccharide) units, by treatment with an oxidant followed by a base, and sometimes by physical means, such as the application of shear forces.

The viscosity of a gum solution is a function of both the size and the shape of the dissolved polymer. Gum preparations of reduced average molecular weights have reduced thickening capacity. Industrial gums are usually available in a range of viscosity types for different applications. If thickening is the primary objective, a high viscosity grade gum at low concentration is used. However, if binding, protective colloid action, film formation, or a firm gel is desired, a lower viscosity type of the same gum at a higher concentration is used.

The physical properties of gums, which determine their functional properties, are determined by the chemical nature of the gum molecules, the nature and amount of solvent [water or an aqueous solution (its pH and the presence of dissolved salts, sequestrants, and other solutes)], and their tendency to interact with other molecules (self-association or with other molecules in the system, especially other polymer molecules). Other controlling variables that affect the properties that gums impart to aqueous systems include concentration, shear rate during dispersion, shear rate during use, and temperature.

The rheology of gum solutions is a function of the size, shape, flexibility, ease of deformation, and solvation of the polysaccharide molecules or aggregates of them and the presence and magnitude of charges. Most solutions of industrial gums exhibit shear thinning, ie, they are pseudoplastic, occasionally thixotropic. The variables that affect their rheology are polymer structure, molecular weight, concentration, shear rate, temperature, pH, and the concentration of salts, other solutes, and sequestrants. Factors that affect dispersion and dissolution are pH, presence of salts, presence of other solutes, gum type, particle size, physical form of particles, shear rate, and method of dispersion (mixing efficiency).

In short, properties of gums are manifestations of their chemical structures and the shapes of their molecules or of aggregates containing gum molecules in various states of solvation (hydration). All applications of gums depend on the properties provided by their polymer molecules by themselves or in interaction with each other or other substances. Because the functional properties of gums are determined by the sizes, shapes, and physical properties of their hydrated molecules or clusters of molecules, and because these parameters are functions of both their chemical structures and molecular weights, various functional types of any given gum are produced by controlling the source, the preparation procedure, the derivatization method (if applicable), and any subsequent treatments and modifications.

Because all gums are thickeners and modifiers of the rheology of aqueous systems, the choice of a gum for a particular application often depends on its other characteristics, such as those that allow it to provide body and bulk, to form gels, to absorb and bind water, to be used in coatings, to be used as adhesives, binders, chelaters, crystallization inhibitors, clarifying agents, cloud agents, emollients, emulsifiers, emulsion stabilizers, encapsulating materials, film formers, flocculating agents, foam stabilizers, humectants, protective colloids, suspending agents, suspension stabilizers, swelling agents, syneresis inhibitors, texturing agents, whipping agents, and others.

Solutions of completely linear polysaccharides and linear polysaccharides with short side chains are much more viscous than solutions of highly branched, branch-on-branch polysaccharides of the same molecular weight and concentration. Essentially linear polymers also have more desirable rheological properties, such as pseudoplasticity (shear thinning), and they are better film formers. Essentially linear polymers are generally required for gel formation.

Gums are tasteless, odorless, and colorless. All gums are subject to microbiological attack and are, therefore, biodegradable.

4. Source, Preparation, Properties, and Applications of Specific Gums

The most widely used, nonstarch-based, water-soluble gums are described briefly in the order in which they are presented in Table 1. Dextrins and pregelatinized starches, starch ethers, starch esters, oxidized starches, etc, are not described, although as commercial water-soluble polysaccharide products, they meet the definition of gums.

5. Guar and Locust Bean Gums (Galactomannans)

Guaran, the purified polysaccharide from guar gum, is a polymer of D-galactosyl and D-mannosyl units. It has a linear mannan (the name for a polysaccharide containing only mannosyl units as its monomer units) backbone with an average of about 1 of every 1.8 mannosyl units substituted with an α-D-galactopyranosyl unit. Its average molecular weight is ~220,000 (DP ~1360).

Locust bean (carob) gum is, like guaran, a galactomannan [11078-30-1], and has a similar structure. However, in locust bean gum, ~1 of every 3.9 β-D-mannopyranosyl units, on average, is substituted with an α-D-galactopyranosyl unit. The locust bean gum molecule contains backbone regions that contain no D-galactopyranosyl units and regions in which most main-chain units contain single-unit α-D-galactopyranosyl branches. Its average molecular weight is ~330,000 (DP ~2000).

Commercial guar gum is the ground endosperm of guar seeds. Guar endosperm preparations can be modified via reactions of its hydroxyl groups (as can any other polysaccharide). Derivatives (Table 1) are made to control its rate of hydration, peak viscosity, ash content, insoluble material, heat stability, and compatibility with other materials. Guar gum forms very high viscosity, pseudoplastic (instantaneously shear thinning) solutions at low concentrations. Because commercial guar gum contains protein, fiber, and lipids, its solutions are always cloudy. Polymer chains of guar gum and its derivatives, because both of its monosaccharide units contain cis-diol groups, can be cross-linked with borate and titanium ions, a property very useful in petroleum production by hydraulic fracturing. Gels formed in this way are rubbery. Guar gum is used in food products. Guar gum or modified guar gum products are used in textile printing pastes, to thicken and gel blasting agents and explosive slurries, in water and water–methanol-based fracturing fluids for oil and gas wells, as processing aids in the separation of certain minerals from their ores, and in fabric softeners. For nonfood applications, guar gum and modified guar gum products are often sold with additives that control the rate of hydration, resistance to enzymes, dispersibility, or flow properties of the dry powder.

Like guar gum, commercial locust bean gum (LBG) is the ground endosperm of the seeds of the locust bean (carob) tree. Locust bean (carob) gum has low cold-water solubility and is used when delayed viscosity development is desired. High viscosity is obtained only when dispersions of locust bean gum are heated (eg, to 85°C) and cooled. The general properties of LBG are similar to those of guar gum. Differences are its low cold-water solubility and its synergism with κ-carrageenan, furcellaran, and xanthan. Locust bean gum is used primarily in food products, often making use of the gel-forming ability of mixtures of LBG and κ-carrageenan or xanthan.

6. Algins/Alginates

Algins are linear, anionic polysaccharides with block copolymer structures. They are salts (generally sodium [9005-38-3], ammonium [9005-34-9], or potassium [9005-36-1]) or propylene glycol esters of alginic acid [9005-32-7], alginic acid being a generic term for copolymers of D-mannuronic acid and L-guluronic acid units. Ratios of the constituent monomers and chain segments vary with the source and determine the specific properties of the preparation. The degree of polymerization (molecular weight) is controlled and varied in commercial products.

Algins are extracted from brown algae. The polymer is extracted by treating the seaweed with a sodium carbonate solution. It is recovered from the extract by precipitation as alginic acid or as the calcium salt, both of which are insoluble in water. In the latter case, the calcium salt is subsequently converted into alginic acid. Alginic acid is then treated with a base to convert it into the desired soluble salt, or partially neutralized alginic acid is treated with propylene oxide to make the soluble partial propylene glycol ester.

The specific properties exhibited by a solution of an algin preparation depend on the ratio of its monomeric units, the concentration and type of cations in solution, the temperature, and the degree of polymerization. Alginate molecules in aqueous solutions are highly hydrated, linear polyelectrolytes in extended conformations. An important and useful property of alginates is their ability to form gels by reaction with calcium ions. Alginates with a higher percentage of polyguluronate segments form the more rigid, more brittle gels. Alginates with the higher percentage of polymannuronate segments form the more elastic, more deformable gels that have a reduced tendency to undergo syneresis. Sodium alginate is used extensively in textile printing pastes and in gelled food products.

7. Agars, Carrageenans, and Furcellarans

Carrageenan is a generic term applied to polysaccharides extracted from a number of closely related species of red algae. Agar and furcellaran are also red seaweed extracts and are members of the same larger family. All polysaccharides in the larger family are sulfated linear galactans (polysaccharides made up of galactosyl and/or modified galactosyl, ie, 3,6-anhydro-D-galactopyranosyl, monomer units). Commercial carrageenans are composed primarily of three types of polymers: κ-, ι-, and λ-carrageenan. Their molecular weights average ~250,000. The half-ester sulfate contents are 0–3% in agarose, the linear component of agar: 12–16% in furcellaran; ~25% in κ-carrageenan [1114-20-8]; ~32% in ι-carrageenan [9062-07-1]; and ~35% in λ-carrageenan [9064-57-1]. The composition and properties of any preparation is dependent on the species collected, its growth conditions, and the production process. Most carrageenan is used to make gels. Blends of the three general types of carrageenan are often employed, with each preparation usually standardized to a gel characteristic. Most carrageen preparations are used in food products; they are also used in toothpaste and in room freshener gels.

Carrageenans are extracted primarily from *Chondrus* and *Gigartina* species of red algae. Furcellaran is obtained from *Furcellaria* species. Agars are obtained primarily from *Gelidium* and *Gracilaria* species. Carrageenans are extracted from blended seaweeds with hot, slightly alkaline water. The alkalinity aids in extraction of the polysaccharide; it also catalyzes intraunit nucleophilic displacement of 6-sulfate groups by O-3, forming 3,6-anhydro rings.

A useful property of the red seaweed extracts is their ability to form gels with water and milk. Carrageenans are blended and standardized to provide products that will form a wide variety of gels: clear to turbid gels, rigid to elastic gels, tough-to-tender gels, heat stable to thermally reversible gels, gels that undergo syneresis to those that do not. Carrageenan gels do not melt at room temperature, do not require refrigeration, and are freeze–thaw stable. Carrageenans form complexes with proteins. κ-Carrageenan interacts with milk protein micelles, particularly κ-casein micelles; at a concentration of 0.025% in milk, a weak thixotropic gel is formed. There is a synergistic effect between κ-carrageenan and locust bean gum; the two gums together produce a much more elastic gel with markedly greater gel strength and less syneresis.

Because the sulfate half-ester groups have low pK_a values, carrageenans are polyanionic, even in very acidic solutions; but they are also unstable in acidic systems. κ- and ι-Carrageenans exist as right-handed, threefold helices that form double helices reversibly. The double helical segments can then interact to form a 3D gel network. Potassium ions are the most effective for gelling κ-carrageenan solutions. ι-Type carrageenans require calcium ions for gel formation. λ-Type carrageenans are nongelling.

Agars are the least soluble members of this class of polysaccharides. They can be dissolved only at temperatures >100°C. When hot agar solutions are cooled, strong, brittle, turbid gels form. By far the greatest use of agar in the United States is in the preparation of microbiological culture media. Agar is also used in bakery icings because of its nonmelting characteristics and its compatibility with high sugar concentrations. Agarose, the linear component of agar, is used in making gels for electrophoresis, to make media for size-exclusion chromatography, and in several biotechnological applications.

8. Pectins

Pectins are mixtures of polysaccharides that originate from plants, and contain poly(α-D-galactopyranosyluronic acid) molecules [9046-38-2, 84149-03-1, 25249-

06-3] in a partial methyl ester form and various degrees of neutralization as the major components. They are water soluble, and their solutions gel under suitable conditions. Pectins with a degree of esterification (DE; degree of methyl esterification, DM) $>50\%$ are high methoxyl pectins (HM-pectins) [65546-99-8]; those with DE $<50\%$ are low methoxyl pectins (LM-pectins). Amidated pectins are low methoxyl pectins that contain, in addition to carboxylate and carboxyl methyl ester groups, carboxamide groups. They are particularly sensitive to calcium ions. The degree of amidation (DA) indicates the percent of carboxyl groups in the amide form. The DE strongly influences the solubility, gel-forming ability, conditions required for gelation, gelling temperature, and gel properties of the preparation. The commercial importance of pectin is predominantly the result of its unique ability to form spreadable gels (jams, jellies, preserves, etc) in the presence of a solute that competes for water of hydration (almost always sugar) at pH ~ 3, or in the presence of calcium ions. Junction zones are formed between regular, unbranched HM-pectin chains when the negative charges on the carboxylate groups are removed (addition of acid), and the hydration of molecules is reduced (addition of a cosolute such as sugar to an acidic solution of HM-pectin), or polymer chains are bridged by multivalent (eg, calcium) cations (LM-pectin).

9. Gellan

Gellan is a gelling, bacterial polysaccharide produced by specific species of *Sphingomonas*. It is a linear polysaccharide composed of (in the native state) acylated tetrasaccharide repeating units. The native polysaccharide [142804-65-7] can be deesterifed. By varying the degree of acylation, products [71010-52-1] that provide a range of gel textures are made available. The more deacylated products produce the firmer, more brittle gels. Gellan has good thermal stability. Gellan solutions will gel when any cation is present, but divalent cations are much more effective. Dilute solutions of gellan have very good suspending power. A primary use is in plant tissue culture media. Commercially, gellan is called gellan gum.

10. Welan

Welan is a nongelling bacterial polysaccharide produced by a species of *Alcaligenes*. Welan has the same tetrasaccharide repeating unit structure as gellan as a backbone with a single-unit glycosyl substituent on each repeating unit. Like the molecules of gellan, the molecules of welan are acylated.

For a polysaccharide, welan is exceptionally heat stable, and temperature has little effect on its low concentration, high viscosity solutions, even up to 150°C or higher. Welan solutions are also relatively unaffected by pH. They are pseudoplastic, stable in the presence of high concentrations of salt, and good suspension stabilizers. These properties are what is needed for drilling, workover, and completion fluids, particularly in deep oil and gas wells where bottom hole temperatures exceed 120°C.

11. Xanthan

Xanthan (known commercially as xanthan gum) has a main chain identical to the structure of cellulose molecules. However, in xanthan, every other β-D-glucopyranosyl unit in the main chain is substituted with a trisaccharide unit. The molecular weight is probably in the order of 2×10^6, although much higher figures have been reported. The unusual properties of xanthan undoubtedly result from its structural rigidity, which in turn is a consequence of its linear backbone, which is stiffened and shielded by the trisaccharide side chains that more-or-less wrap around it. In solution, it may occur as a single helix, an extended double helix, and a compact double helix; the helices may form side-by-side dimers.

Xanthan is an extracellular (exocellular) bacterial polysaccharide. It is recovered from pasteurized fermentation medium by precipitation, either with or without prior clarification, depending on the desired product. As with other microbial polysaccharides, the characteristics (polymer structure, molecular weight, solution properties) of xanthan preparations are constant and reproducible when a particular strain of *Xanthomonas campestris* is grown under specific conditions, as is done commercially. The gum's characteristics will vary, however, with variations in the strain of the organism and growth conditions.

Xanthan solutions are extremely pseudoplastic and have high yield values, making them almost ideal for the stabilization of aqueous dispersions, suspensions, and emulsions. Whereas other polysaccharide solutions decrease in viscosity when they are heated (with the exception of welan solutions), xanthan solutions containing a low concentration (0.1%) of salt change little in viscosity over the temperature range 0–95°C. Although xanthan is anionic, pH has almost no effect on the viscosity of its solutions over the range pH 1–12. A synergistic viscosity increase results from the interaction of xanthan with galactomannans. The xanthan-locust bean gum combination forms thermally reversible gels when solutions of the two are heated and subsequently cooled.

Xanthan is used in various aspects of petroleum production, including oil well drilling, hydraulic fracturing, and work-over, completion, pipeline cleaning, and enhanced-oil-recovery fluids. It also finds application in a large number and variety of foods and in consumer and agricultural chemical products.

12. Gum Arabic

Of the gums of ancient commerce (gum arabic, gum ghatti, gum karaya, and gum tragacanth), which were dried, gummy exudations collected by hand from various trees and shrubs, only gum arabic, also called arabic gum, gum acacia and acacia gum, is still in significant use. Gum arabic preparations are mixtures of highly branched, branch-on-branch, acidic polysaccharides, the composition of which varies with species, season, and climate. Generally accepted values for number- and weight-average molecular weights are ~250,000 and ~580,000, respectively; these values correspond to DPs of ~155 and ~3600 and indicate a high degree of polydispersity. Gum arabic is unique among gums because of its high solubility and the low viscosity and Newtonian flow of its solutions. While other gum preparations (unless the average molecular weight of the gum has been reduced by depolymerization to form a low viscosity type) form highly viscous solutions at 1–2% concentration, 20% solutions of gum arabic are only slightly viscous. Its main uses in the United States are in the preparation of flavor oil emulsions and dry powders made by spray drying such emulsions, in coating certain confections, and in making encapsulating coacervates for pressure-sensitive transfer record sheets (carbonless copy paper).

13. Cellulose Derivatives

Cellulose [9004-34-6] is derivatized to make both water-soluble gums and hydrophobic, thermoplastic polymers. (The latter are not included here because they are not water soluble and, therefore, not gums.) All water-soluble cellulose derivatives vary in the extent of derivatization, the ratio of substituent groups if more then one, and the average degree of polymerization (average molecular weight). In other words, each type of water-soluble cellulose derivative is itself a family of products, each member of which is tailor made to have specific properties.

Carboxymethylcellulose (CMC) is the sodium salt of the carboxymethyl (glycolic acid) ether of cellulose. To prepare CMC, cellulose is steeped in sodium hydroxide solution, and the so-called alkali cellulose [9081-58-7] is reacted with sodium monochloroacetate to form the sodium salt of carboxymethylcellulose and sodium chloride. Therefore, commercial CMC is sodium carboxymethylcellulose.

The physical properties (solution characteristics) of CMC and all other polysaccharide derivatives are determined by the average chain length or degree of polymerization of the polysaccharide (in this case, cellulose) molecules, the degree of substitution (DS, the average number of substituent groups per glycosyl unit, the maximum number being 3), and the uniformity of substitution. The DS of different CMC types generally ranges from 0.4 to 0.8; some products may approach a DS of 1.5. The most widely used types have a DS of 0.7 or an average of 7 carboxymethyl ether groups/ 10 β-D-glucopyranosyl units. CMC is available in many viscosity grades.

Carboxymethylcellulose hydrates rapidly and forms clear solutions. Imparting viscosity is the single most important property of CMC. Dilute solutions of CMC exhibit stable viscosity because each polymer chain is hydrated, extended, and independent. The sodium carboxylate groups are highly hydrated, and the cellulose molecule itself is hydrated. The cellulose molecule is linear, and conversion of it into a polyanion tends to keep it in an extended form because of Coulombic repulsion. This same Coulombic repulsion between the carboxylate anions prevents aggregation of polymer chains. Solutions of CMC are either pseudoplastic or thixotropic (time-dependent shear thinning), depending on the uniformity of substitution.

Carboxymethylcellulose is useful as a warp size, in a broad spectrum of food products, in cosmetic and personal care products, in oil and gas well-drilling fluids, and in a variety of other applications.

Hydroxyalkylcelluloses are cellulose ethers prepared by reacting alkali cellulose with ethylene oxide [to prepare hydroxyethylcelluloses (HECs)] or propylene oxide [to prepare hydroxypropylcelluloses (HPCs)]. These products are characterized in terms of moles of substitution (MS) rather than DS. Moles of substitution are used because the reaction of an ethylene or propylene oxide molecule with cellulose leads to the formation of a new hydroxyl group with which another alkylene oxide molecule can react to form an oligomeric side chain. Therefore, theoretically there is no limit to the number of moles of substituent that can be added to each D-glucopyranosyl unit. MS denotes the average number of moles of alkylene oxide that has reacted per D-glucopyranosyl unit. In general, the MS controls the solubility of hydroxyalkylcelluloses. For example, water-soluble grades of HEC have MS values of 1.6–3.0; those with MS 0.3–1.0 are soluble only in aqueous alkali. Higher MS types of HPC become soluble in organic solvents: first polar organic solvents, then nonpolar solvents, and are not gums.

Both HEC and HPC form clear, smooth solutions. Both gums, like other cellulose derivatives, are produced in a wide range of viscosity grades, including high viscosity types. Also, like other cellulose ethers, their solutions are Newtonian at low shear rates and become pseudoplastic at higher shear rates. The shear rate at which solutions change from being Newtonian to being pseudoplastic increases with increasing molecular weight and lower concentrations. Also, the higher molecular weight products are more affected by shear. Because they are nonionic gums, the hydroxyalkylcelluloses are unaffected by pH.

Clear, water-soluble, oil- and grease-resistant films of moderate strength can be cast from HEC solutions. Flexible, nontacky, heat-sealable packaging films and sheets can be produced from HPC by conventional extrusion techniques. Both gums can be used in the formulation of coatings, even edible films and coatings. The primary use of HEC is for thickening latex paint. Hydroxyethylcellulose is also used as a protective colloid in the production of vinyl acetate homopolymer latexes and for acrylic emulsions, in both dry and ready-to-use joint cements for wallboard, in adhesives, in high salt drilling muds, in sustained-release formulations, and in a variety of other applications and products. Hydroxypropylcellulose is used as a secondary stabilizer in suspension polymerization of vinyl chloride and as a granulating agent for pharmaceutical tablet and capsule mixes.

In methylcelluloses, some of the hydroxyl groups along the cellulose molecule have been converted into methyl ethers. Hydroxyalkylmethylcelluloses contain, in addition to methoxyl groups, hydroxyalkoxyl groups in place of some of the hydroxyl groups. The properties of methyl- and hydroxyalkylmethylcelluloses are also a function of the type(s) of derivatization, the amount of each type of substituent group, the molecular weight distribution of the polymer molecules, and to some extent, the physical nature of the product (eg, fibrous vs. powdered, mesh size, surface treatment). Because these variables can be controlled to some degree, the members of this methylcellulose family are tailor-made products, as are other cellulose derivatives.

Methylcelluloses are made by reacting alkali cellulose with methyl chloride until the DS reaches 1.1–2.2. Hydroxypropylmethylcelluloses (HPMCs) are made by using propylene oxide in addition to methyl chloride in the reaction; MS values of the hydroxypropyl group in most commercial HPMCs are 0.02–0.3. Use of 1,2-butylene oxide in the alkylation reaction mixture gives hydroxybutylmethylcelluloses (MS 0.04–0.11). Hydroxyethylmethylcelluloses are made with ethylene oxide in the reaction mixture. All members of this family of substances are generally termed methylcelluloses even though they may also contain hydroxyalkyl groups.

Conversion of some of the hydroxyl groups of cellulose molecules into methyl ether groups increases the water solubility of the cellulose molecule and reduces its ability to aggregate, ie, reduces intermolecular interactions. Solubility is increased even more when hydroxyalkyl groups are added to methylcellulose. Solutions of all these products behave somewhat like those of guar and locust bean gums, ie, as linear polysaccharides with short side chains that give stable solutions of high viscosity. As substituent groups are added, the solubility of the products changes from being insoluble to soluble in aqueous alkali, to soluble in water, to soluble in various polar organic solvents, such as water–alcohol solutions, alcohols, and alcohol–hydrocarbon solutions.

The most interesting property of these nonionic products is thermal gelation. Solutions of members of this family of gums that are soluble in cold water decrease in viscosity when heated, like solutions of other polysaccharides. However, unlike other gum solutions (except those of curdlan), when a certain temperature is reached, the solution viscosity increases rapidly and the solution gels. Gelation can occur from $\sim$45 to $\sim$90°C, depending on the viscosity type, DS or MS, and the proportions of methyl and hydroxyalkyl substituent groups. The thermal gelation is reversible. (That of solutions of curdlan is not.)

Surfactants greatly increase the viscosity of methylcellulose solutions. Methylcelluloses reduce surface and interfacial tension. Methylcelluloses will form high strength films and sheets that are clear, water-soluble, and oil- and grease-resistant and have low oxygen and moisture vapor transmission rates. The main use of methylcelluloses is in the preparation of tape-joint compounds for gypsum board paneling, in gypsum spray plaster, and in ceramic tile adhesive, grout, and mortar formulations. They are also used in ceramics, food products, wallpaper adhesives, shampoos, and a variety of other applications.

As mentioned earlier, non-water-soluble cellulose derivatives, such as cellulose diacetate (acetate rayon) and ethylcellulose, are not considered to be gums.

14. Summary of Properties

As mentioned earlier, the common property of industrial gums is their ability to increase the viscosity of, ie, to thicken, aqueous systems at low concentrations (generally $<2\%$). Some unique properties are listed in Table 2.

15. General Applications

Below are a few examples of general applications of water-soluble gums:

Adhesives: billboard, corrugating, remoistenable, wallpaper.
Agriculture: encapsulation of pesticide formulations.
Biotechnology: microbiological and cell culture media.

Table 2. **Selected Gums and Their Unique Properties**

Gum	Unique property
agar	gels require high temperatures for remelting. Gels are compatible with high solute concentrations
algins/alginates	gelation with Ca^{2+}
propylene glycol alginates	surface activity
carboxymethylcelluloses	form clear, stable, either pseudoplastic or thixotropic solutions
κ-type carrageenans	gelation with K^+. Form complexes with proteins, especially milk proteins, forming soft, thixotropic gels. Form gels via synergistic interaction with locust bean gum
ι-type carrageenans	gelation with Ca^{2+}
curdlan	irreversible thermogelation
gellans	form gels with a range of textures with any cation. Good suspension stabilizers
guar gum	gelation with borate and titanium ions
gum arabic	low solution viscosity at high concentrations. Newtonian flow of solutions of up to 50% concentration. Both an emulsifier and an emulsion stabilizer. Emulsions can be spray-dried without conditioning air
hydroxyethylcelluloses	form clear, water-soluble, oil- and grease-resistant films and coatings
hydroxypropylcelluloses	form non-tacky, heat-sealable packaging films
locust bean (carob) gum	gelation via synergistic interactions with κ-carrageenan and xanthan
methylcelluloses, including hydroxypropylmethylcelluloses	reversible thermogelation. Soluble in cold water; insoluble in hot water
high methoxyl pectins	form spreadable gels with ~65% sugar and a solution pH of ~3
low-methoxyl pectins	gelation with Ca^{2+}, ie, without sugar and acid
amidated pectins	gelation with very low concentrations of Ca^{2+}
welan	very thermal stable. Very good suspension stabilization. Solutions will tolerate high concentrations of salts
xanthan	solutions are highly pseudoplastic. Temperature has no effect on solution viscosity from 0 to 95°C. Stable in highly acidic systems; pH has no effect on solution viscosity from pH 1 to 12. Synergistic thickening with guar gum. Synergistic gelation with locust bean gum. Very good emulsion and suspension stabilization. Imparts freeze–thaw stability to products

Ceramics: binders, glazes, slip agents.

Construction: gypsum spray plaster formulations, cement formulations, tape joint compounds.

Cosmetics: stabilizers, film formers, and emollients in creams and lotions.

Explosives: water-resistant gel formation.

Processed foods: bakery products, beverages, breakfast cereal products, confectionary products, dairy products, dietetic foods, dry mixes, noncook pie fillings, dry flavor powders, frozen foods, icings, jams, jellies, processed meat products, pet foods, preserves, noncook puddings, pourable salad dressings, sauces, spreads, syrups, toppings, whipped products.

Metal working: refractory coating formulations.

Mining and minerals: flocculation of particles, depression of slimes.

Oil and gas production: cementing, drilling fluids, fracturing fluids, enhanced oil recovery, pipeline cleaning, workover fluids, completion fluids, packer fluids.

Paint: latex paint thickener.

Personal care products: creams, denture adhesives, lotions, ointments, shampoos, toothpastes.

Pharmaceutical and related applications: dental impression material, granulating agents, plasma volume expander, sustained release agents, tablet binders, tablet coatings, tablet excipients, treatment for constipation, treatment for diarrhea, wound-healing fibers.

Polymer production: suspension and emulsion polymerization adjuncts.

Printing: ink thickeners.

Textile: printing pastes.

Tobacco: reconstituted sheet.

Wildfire control: rheology modifier, ignition retardation, foam stabilization.

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