Structure-property Correlations of Non-starch Food Polysaccharides

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SUMMARY: Gums, the majority of which are polysaccharides, have a wide variety of chemical structures, a range of physicochemical properties, and impart a range of functionalities to foodstuffs and prepared foods.

This paper served as an introduction to the symposium. As a brief overview, it is restricted in its scope. (1) Only polysaccharides are discussed. Omitted are proteins – the other major class of biopolymers that impart functionality to foods and food products. With the principal exception of gelatin and the lesser use of soy protein concentrate and soy protein isolate, most protein in food products comes from adding a whole, complex ingredient such as milk, eggs, and/or flour. (2) The focus is on general structures and physicochemical properties, rather than amounts sold or specific products.

Water-soluble and water-dispersible polysaccharides used as food additives or processing aids are known as gums or hydrocolloids (as are the proteins used in the same way). At low concentrations in water, gums generally produce viscous solutions and, in some cases, gels. Gums are used in foods (1) to correct or minimize a defect, i.e., to improve the appearance, body, texture, or stability of a food product; (2) to develop new products, e.g., more convenient or more healthful products; and (3) to allow use of new processes and/or processing equipment. Improved stability might result from a particular functionality, e.g., chelation of a specific metal ion.

Structures and Classifications

Food gums and other polysaccharides can be, and are, classified by source, by structure, and by composition. No one scheme is completely satisfactory. Table 1 gives a classification by

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source of the primary food gums. Included are starches and modified starches. Starches satisfy the definition of gum, but are usually considered separately because of their overwhelming volume of use and special characteristics, primarily the fact that starches occur as granules. Table 2 gives a classification by polymer structure. Since most whole starches are a binary mixture of polysaccharides, they are not included. Neither are those polysaccharides that may be important determinants of food functionalities, but which are not added as isolated ingredients. The latter include, but are not limited to, hemicelluloses and pentosans such as xylans and arabinoxylans, arabinogalactans, xyloglucans, psyllium seed gum, okra gum, and native starches. Table 3 gives a classification of gums based on the number of different kinds of monosaccharide units in their structures. The same restrictions imposed on Table 2 apply to Table 3.

Table 1. Classification of Selected Food Polysaccharides by Source

Source	Examples
Algal (seaweed extracts)	Agars, algins, carrageenans, furcellaran
Higher plants	
Insoluble	Cellulose
Extract	Pectins
Seeds	Corn starches, rice starches, wheat starch, guar gum, locust bean gum
Tubers and roots	Potato starch, tapioca starch, konjac mannan
Exudates	Gum arabics, gum tragacanth
Microorganisms (fermentation gums)	Xanthans, gellan, curdlan
Derived	
From cellulose	Carboxymethylcelluloses (CMC), hydroxypropylcelluloses (HPC), hydroxypropylmethylcelluloses (HPMC), methylcelluloses (MC)
From starch	Starch acetates, starch 1-octenylsuccinates, starch phosphates, starch succinates, hydroxypropylstarches, dextrins
Synthetic	Polydextrose

Table 2. Classification of Selected Food Polysaccharides by Structure

Classification Schemes	Examples
By shape	
Linear	Agars (agaran/agarose), algins, amyloses, carrageenans, cellulose, curdlan, furcellaran, gellan, inulin, CMC, MC, HPMC, HPC
Branched	
Short branches on a linear backbone	Curdlan, galactomannans, (guar gum, locust bean gum), konjac mannan, xanthan
Branch-on-branch structures	Amylopectins, gum arabics, gum tragacanth (tragacanthin)
By charge	
Neutral	Agars (agaran/agarose), amylopectins, amyloses, cellulose, curdlan, galactomannans, inulin, konjac mannan, MC, HPMC, HPC
Anionic (acidic)[a]	Algins, carrageenans, curdlan, xanthan, gellan, gum arabics, gum tragacanth (tragacanthin), pectins/pectates, CMC

[a] From the presence of uronic acid, sulfate half-ester, pyruvyl cyclic acetal, or succinate half-ester groups.

Table 3. Classification of Selected Unmodified Food Polysaccharides by Composition

Classification Schemes	Examples
By monomeric units[a]	
Homoglycans	Amylopectins, amyloses, cellulose, curdlan
Diheteroglycans	Agars (agaran/agarose), algins, carrageenans, furcellaran, galactomannans, konjac mannan
Triheteroglycans	Gellan, xanthan
Tetraheteroglycans	Gum arabics
Pentaheteroglycans	Gum tragacanth (tragacanthin)

[a] Considers only the basic monosaccharide units. A derivatized monosaccharide unit, such as a D-galactopyranosyl 6-sulfate unit, is not considered as a unit separate from a D-galactopyranosyl unit, for example.

Individual sugars/monosaccharides, the monomeric building blocks of polysaccharides, lend themselves to a great variety of polymeric structures. In polysaccharides, the sugars are in a ring form, most often a six-membered ring, the pyranose ring. Considering only aldohexose units in pyranose rings linked head-to-tail by glycosidic linkages, 8 different disaccharides can be formed from a single sugar, and 16 different disaccharides can be formed from two different sugars. Identical aldohexopyranosyl units linked head-to-tail can form 64 different trisaccharide structures; three different aldohexopyranosyl units can form 384 different trisaccharides. Polysaccharides contain from hundreds to hundreds of thousands of monosaccharide units. Eleven different kinds of monosaccharide units most commonly occur in the gums of commerce. Both pyranose and furanose (the five-membered) ring forms, all possible head-to-tail linkages, and both anomeric configurations of these monosaccharide units are found, and because carbohydrates are polyhydroxy compounds, branching can, and does, occur. Segments of polysaccharide molecules showing some different general structures are given in Figure 1.

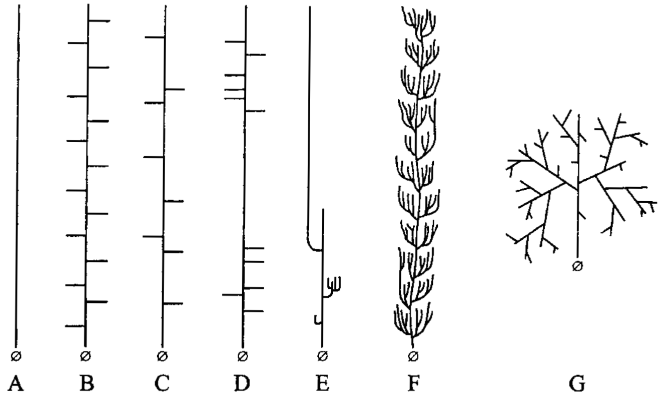

Fig. 1: Portions of polysaccharide molecules showing the variety of general structures occurring in nature. ϕ = reducing end of the polymer. A = unbranched, linear structure as in cellulose and algins. B,C,D = short branches on a linear backbone; B = regularly spaced branches as in xanthan, C = irregularly spaced branches as in guar gum, D = clustered branches as in locust bean gum, E = few, very long branches as in amylose, F = clustered branches as in amylopectin, G = branch-on-branch structure as in gum arabic.

Bacterial polysaccharides (the fermentation gums) often contain regular repeating units, although post-polymerization modifications (by esterification, for example) can result in variability in the repeating-unit structure.

Plant polysaccharides do not have uniform, repeating-unit-type structures; rather they are polymolecular, i.e, their structures vary from molecule to molecule. In addition, the average structure can vary with the source and the environmental conditions experienced by the land or sea plant. While linear glycans are the most abundant in nature because of the enormous quantity of cellulose existing as the main structural element of the cell walls of higher land plants, branched polysaccharides are by far the most numerous, occurring in an variety of branched structures and with a variety of sugars in their structures. Some polysaccharides are neutral; some are anionic (Table 2). Some are linear; some are branched (Table 2). Some of the branched polysaccharides are still effectively linear; some are bush-like (Fig. 1). Some contain, in addition to sugar units, ether, ester, and/or cyclic acetal groups, either naturally or as a result of chemical modification. Some are soluble in cold water; some are soluble only in hot water, and some require aqueous solutions of acids, bases, or metal ion-chelating compounds to extract them from the plant tissue. Some, like cellulose, are insoluble in anything but special solvents.

Preparations of native polysaccharides always are polydisperse (composed of a mixture of molecules with a range of molecular weights); commercial gums often are even more polydisperse because they often are depolymerized to some extent to produce different viscosity grades. The number of monosaccharide units in a polysaccharide, termed its degree of polymerization (DP), varies with polysaccharide type. Only a few polysaccharides have a DP less then 100; most have DPs in the range of 200-3,000. Larger molecules, like those of cellulose, have DPs of 7,000-15,000. Amylopectin molecules may have DPs of $>10^6$ and molecular weights of $>10^8$. So polysaccharides present a variety of chemical structures, molecular weights, and solubilities; and most polysaccharides have both inter- and intramolecular heterogeneity.

Properties, Applications, and Modifications

The usefulness of food gums is based on their physical properties, in particular their capacity to thicken and/or gel aqueous systems and otherwise to control water. Because all gums modify the flow of aqueous solutions, dispersions, and suspensions, the choice of which gum to use for a particular application often depends on its secondary characteristics. These secondary characteristics are responsible for their utilization as binders, bodying agents, bulking agents, crystallization inhibitors, clarifying agents, cloud agents, emulsifying agents, emulsion stabilizers, encapsulating agents, film formers, flocculating agents, foam stabilizers, gelling materials, mold release agents, protective colloids, suspending agents, suspension stabilizers, swelling agents, syneresis inhibitors, texturing agents, and whipping agents, in coatings, and for water absorption and binding. Most gums are not true emulsification agents, but stabilize emulsions and suspensions by increasing the viscosity and the yield value of the aqueous phase. Some also exhibit protective colloid action.

Food gums are tasteless, odorless, colorless, and non-toxic. All (except the starches, starch derivatives, and gelatin) are nondigestible and, therefore, essentially noncaloric. Nondigestible gums are classified as soluble fiber.

Three-dimensional shapes of polysaccharides in solution generally are those of helical, wormlike chains (between completely helical and a random coil) or stiff coils (between a rigid rod and a random coil). They are generally not in the form of compact spheres, like most globular proteins are. Some, such as guaran (the polysaccharide of guar gum), approach being random coils.

In general, gum solutions exhibit shear thinning; they are usually pseudoplastic, occasionally thixotropic. Variables that affect the rheology of their solutions are polymer structure, molecular weight, concentration, shear rate, temperature, pH, and concentrations 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). Most gums are available in a range of viscosity grades.

In general, food gum gels are composed of at least 99% water and less than 1% gum. Gels are continuous, three-dimensional networks of connected polymer molecules or particles entrapping a large volume of a continuous liquid phase. They are formed from polymers (polysaccharides or proteins) when molecules or bundles of molecules form at least two associations over limited portions of their lengths by hydrogen bonding, hydrophobic interactions, or ionic cross-bridges or simply entangle, in either case forming a three-dimensional network that fills the entire container. Types of junction zones are outlined in Table 4. Intermolecular interactions of molecules in junction zones are described in the second paper of the symposium by Chandrasekaran. Ways that gum solutions can be changed into gels are given in Table 5. Important characteristics of gels are means of gelation (chemical gelation, thermal gelation), reversibility (temperature, shear), texture (brittle, elastic, plastic), rigidity (rigid or firm, soft or mushy), tendency for syneresis, and cutable or spreadable.

Table 4. Types of Junction Zones Involving Polysaccharides

1. Intermolecular interactions between regular, linear segments of molecules of the same polysaccharide.
2. Intermolecular interactions between regular, linear segments of polyanionic polysaccharide molecules effected by cations.
3. Interactions between ionic polysaccharide molecules and protein molecules.
4. Interactions between linear chain segments of two different polysaccharide molecules.
5. Chain entanglements.
6. Crosslinking of neutral polysaccharide molecules with a multivalent anion (non-food).

Table 5. Formation of Polysaccharide Food Gels

Gelling Conditions	Polysaccharides
With acids	Sodium alginates High-DM pectins + sugar
With cations	
• with any cation	Gellan
• with calcium ions	Sodium alginates Iota-type carrageenans Low-DM pectins
• with potassium ions	Kappa-type carrageenans
• with proteins	Carrageenans (above pI of protein) Carrageenans + pectin (below pI of protein)
Upon cooling of hot solutions	Agar Calcium alginates Gellan High-DM pectins + acid + sugar Calcium pectinates Kappa-type carrageenans + locust bean gum Xanthan + kappa-type carrageenans Xanthan + locust bean gum Xanthan + agarose Starches
Upon heating of solutions	Curdlan (irreversible) Hydroxypropylmethylcelluloses (thermoreversible) Methylcelluloses (thermoreversible)
With addition of solutes	High-DM pectins + acid
Shear-reversible gels	Iota-type carrageenans (above pH 5.0, 20-80 Brix) Low-DM pectins (below pH 5.0, 20-80 Brix)

Polysaccharides are essentially polymers containing primary and secondary hydroxyl groups; sometimes the primary hydroxyl group is replaced with a carboxyl group. Thus, polysaccharides undergo reactions of hydroxyl groups and of carboxyl groups, if present. Reactions used commercially to modify polysaccharides are given in Table 6. Modifications are effected to enhance positive attributes or to minimize negative ones. A few native and modified polysaccharide gums are described below.

Table 6. Polysaccharide Modification

By Chemical Reaction

- Derivatization
  - etherification of hydroxyl groups (cellulose, starches)
  - esterification of hydroxyl groups (starches)
  - esterification of uronic acid carboxyl groups (algins)
  - amidation of uronic acid carboxyl groups (LM-pectin)

- Depolymerization
  - via acid-catalyzed hydrolysis (starches and gums in general)
  - via beta-eliminations (cellulose, following oxidation)

- Oxidation (starches)

- Transglycosylation (starches)

- Deacylation
  - of uronic acid esters (pectin)
  - of hydroxyl group esters (konjac mannan)

Genetically

- Current
  - via selection and breeding (starches)
  - via mutant production and/or selection and breeding (starches)

- Future
  - via gene transfer
    - synthases (potato starch)
    - branching and debranching enzymes
    - derivatizing enzymes
      - via regulation control (potato starch)

By Growth Conditions (natural)

- controlled environments

By Physical Means

Carboxymethylcelluloses

Cellulose is a linear glucan (Fig. 1A). Carboxymethylcellulose (CMC) is the sodium salt of the carboxymethyl ether of cellulose. Modified polysaccharides, such as CMC, have a degree of substitution (DS). The average number of hydroxyl groups derivatized (with a carboxymethyl ether group in the case of CMC) per monomeric unit is the DS; the maximum DS of a cellulose derivative is 3 because there are three available hydroxyl groups per β-D-glucopyranosyl unit. The solution characteristics of CMC are primarily determined by the DS, the average chain length (DP), and the uniformity of substitution. The most widely used types of CMC have a DS of 0.7 or an average of 7 carboxymethyl groups per 10 β-D-glucopyranosyl units. Several viscosity grades of CMC are manufactured.

Carboxymethylcelluloses hydrate rapidly and form clear, stable solutions. Viscosity building is their most important property. Solutions can be either pseudoplastic or thixotropic, depending on the type of product used. Solutions are stable over a wide pH range (pH 4-10). As the pH drops below 4, viscosity increases significantly.

Methylcelluloses and Hydroxypropylmethylcelluloses

Methylcelluloses (MC) contain methoxyl groups in place of some of the hydroxyl groups along the cellulose molecule. Hydroxypropylmethylcelluloses (HPMC) contain, in addition to methyl ether groups, hydroxypropyl ether groups along the cellulose chain. The properties of methyl- and hydroxypropylmethylcelluloses are primarily a function of the amount of each type of substituent group and the molecular-weight distribution.

Methylcelluloses are made by reacting cellulose with methyl chloride until the DS reaches 1.1-2.2. Hydroxypropylmethylcelluloses are made by using propylene oxide in addition to methyl chloride in the reaction; hydroxypropyl group MS levels in commercial products are 0.02-0.3. (MS refers to molar substitution, which is the average number of moles of substituent added to a glycosyl unit. It is used because substituent chains can form when propylene oxide is the reactant.)

Members of this family of gums are cold-water soluble. 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, i.e., reduces intermolecular interactions. Solubility and solution stability are increased even more when hydroxypropyl groups are added to methylcelluloses.

The most interesting property of these nonionic products is thermal gelation. Solutions of members of this family of gums decrease in viscosity when heated, as do solutions of most other polysaccharides. However, unlike solutions of other gums, when a certain temperature is reached (depending on the specific product), the viscosity increases rapidly and the solution gels.

Xanthan

Xanthan (also know as xanthan gum) is a widely and extensively used food gum. It is the extracellular polysaccharide produced by *Xanthomonas campestris.* Its characteristics vary with variations in the strain of the organism and fermentation conditions.

Xanthan has a linear main chain that has the same structure as does cellulose. In xanthan, every second β-D-glucopyranosyl unit of the cellulosic backbone is substituted with a trisaccharide unit (Fig. 1B). About half of the trisaccharide side-chain units carry a terminal pyruvic acid cyclic acetal group.

Xanthan solutions are extremely pseudoplastic and have high yield values. These properties make xanthan almost ideal for the stabilization of aqueous dispersions, suspensions, and emulsions.

While other polysaccharide solutions decrease in viscosity when they are heated, xanthan solutions containing a small amount 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.

A synergistic viscosity increase results from the interaction of xanthan with κ-type carrageenans, methylcelluloses, locust bean gum, and konjac mannan. The latter two combinations form thermally reversible gels when hot solutions of these polysaccharides are cooled.

Algins

Algins (alginates) are extracted from brown algae. Algins are salts (generally sodium) or propylene glycol esters of alginic acid. Alginates are linear, block copolymers (Fig. 1A). In alginic acid molecules, at least three different types of polymer segments exist; poly(β-D-mannopyranosyluronic acid) segments, poly(α-L-gulopyranosyluronic acid) segments, and segments with alternating sugar units. The ratios of the constituent monomers and the chain segments vary with the source. The specific properties of algins depend on the percentage of each type of building block.

An important and useful property of alginates is their ability to form gels on interaction with calcium ions. Different types of gels are formed with alginates from different sources. Alginates with a higher percentage of poly(guluronic acid) segments form more rigid, more brittle gels that tend to undergo syneresis. Alginates with a higher percentage of poly(mannuronic acid) segments form more elastic, more deformable gels that have a reduced tendency to undergo syneresis.

Algin solutions are pseudoplastic and exhibit shear thinning over a wide range of shear rates. Solutions of propylene glycol alginate are somewhat thixotropic and are much less sensitive to pH and polyvalent cations. The specific properties exhibited by an algin solution depend on the ratio of monomeric units, the concentration and type of cations in solution, the temperature, and the degree of polymerization.

Carrageenans and Other Members of the Red Seaweed Family of Gums

Carrageenan is a generic term applied to polysaccharides extracted from a number of closely related species of red seaweed; agar and furcellaran are also red seaweed extracts and are members of the same larger family. All polysaccharides in this family are derivatives of linear galactans; all have alternating monosaccharide units and linkages. In agar, the monosaccharide units are β-D-galactopyranosyl and 3,6-anhydro α-L-galactopyranosyl units. In furcellaran and κ- and ι-carrageenans, they are β-D-galactopyranosyl and 3,6-anhydro-α-D-galactopyranosyl units. λ-Carrageenan contains α- and β-D-galactopyranosyl units. Agar contains little or no sulfate half-ester groups. Other members of the family are sulfated: in increasing order, furcellaran (~14%), κ-(~25%), ι-(~30%), λ-(~35%) carrageenan. None of these polymers contains an exact repeating unit structure. Agar is the least soluble member of this family of polysaccharides, and λ-carrageenan the most soluble. Agar forms the strongest gels. λ-Carrageenan does not gel; it is the only member of this family that is nongelling.

Commercial carrageenans are composed primarily of the three types of polymers: κ-, ι-, and λ-carrageenans. The composition and properties of any preparation is dependent on the species collected, their growth conditions, the mixture of species (if any) extracted, and the treatment during production. Products may also be blended. Most products are standardized with respect to any of several properties to produce specific products for specific applications.

Pectins

Commercial pectins are mixtures of polysaccharides that originate from plant cell walls, that contain partially methyl esterified poly(α-D-galactopyranosyluronic acid) as the major component, that are water soluble, and whose solutions will gel under suitable conditions. Pectins are subdivided according to their degree of esterification (DE), a designation of the percentage of carboxyl groups esterified with methanol. Pectins with DE >50% are high-methoxyl (HM) pectins; those with DE <50% are low-methoxyl (LM) pectins. In some LM pectins, termed amidated pectins, some carboxyl groups have been converted into carboxamide groups.

The principal and key feature of all pectin molecules is a linear chain of α-D-galactopyranosyluronic acid units. In all commercial pectins, some of the carboxyl groups are in the methyl ester form; some or all the remaining carboxylic acid groups may be in a carboxylate salt form. In amidated pectins, some will be 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.

Pectins are soluble in hot water. The importance of pectin is predominately the result of its unique ability to form spreadable gels when a hot solution is cooled. HM pectin gels are formed by the addition of sugar to a hot, acidic (pH ~3) solution of pectin in a fruit juice. LM pectins will gel only in the presence of calcium ions. Increasing the concentration of calcium ions increases the gelling temperature and gel strength.

Pectins are examples of fine tuning the properties of a gum. In the case of commercial pectins, it is done by controlling the source of the natural polysaccharide, the isolation/preparation process, the average molecular weight, and the ratio of $-COOH$, $-COO^-$, and $-CONH_2$ groups.

Galactomannans

Commercial guar gum is the ground endosperm of seeds of the guar plant. Guaran is the purified polysaccharide from guar gum. It has a linear backbone chain of β-D-mannopyranosyl units, approximately every other unit of which (on the average) is substituted with an α-D-galactopyranosyl unit. The mannan chain is rather evenly substituted with D-galactopyranosyl units, but the substitution is rather random (Fig. 1C).

Locust bean (carob) gum is also a galactomannan. Like guaran, it has a linear mannan backbone. However, in locust bean gum, only approximately one out of four β-D-mannopyranosyl units is substituted with an α-D-galactopyranosyl unit. The locust bean gum molecule contains "smooth" regions that contain no α-D-galactopyranosyl side-chain units and "hairy" regions in which most main-chain units contain single-unit α-D-galactopyranosyl branches (Fig. 1D). Commercial locust bean gum is the ground endosperm of the seeds of the locust (carob) tree.

Guar gum forms very high viscosity, pseudoplastic solutions at low concentrations. Because guar gum is nonionic, the viscosity of its solutions is not affected greatly by pH.

Locust bean gum has low cold-water solubility and is often used when delayed viscosity development is desired. Only when dispersions of locust bean gum are heated [e.g., to 85°C

(185°F)] and cooled is high viscosity obtained. The general properties of locust bean gum are similar to those of guar gum. A difference is its synergism with κ-carrageenan, furcellaran, and xanthan, with which it forms gels.

References

Several books that present the polysaccharide gums and gelatin are available. Included are the following. More specialized books are also available.

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