Part A
Food Structure Development: The Interplay Between Processing Routes and Formulation Elements

CHAPTER 1

The Role of Hydrocolloids in the Development of Food Structure

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1.1 Introduction and Hydrocolloid Applications in Food Systems

Hydrocolloids are a class of food ingredients that are widely used in the development of food structure. Generally speaking, we can define *hydrocolloids* most simply as water-soluble polymers that contribute viscosity and gelation in solution.[1] ''Gums'' and ''mucilages'' are often used as synonyms. Most hydrocolloids are polysaccharides, but some proteins can also fall into this definition, *e.g.* gelatin and some milk-, egg-, and vegetable-derived protein isolates. However, not all food polysaccharides are hydrocolloids since many of the insoluble polysaccharides, such as unmodified cellulose, do not interact with water. Also, not all water-soluble polysaccharides contribute viscosity due to their molecular weight or molecular structure, *e.g.* the various oligosaccharides or the highly branched dextran, and thus are not considered as hydrocolloids in the conventional use. Granular starch

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may not act as a true hydrocolloid, but gelatinized and other modified starches certainly do. For the sake of clarity, we should also distinguish hydrocolloids from other food colloids. A *colloid* is defined in physical chemistry as a system made up of continuous and dispersed phases in which there is a discrete change in physical properties (*e.g.* density, optical properties) at the phase boundary.[1] Most food colloids are emulsions or foams. A solution or dispersion of hydrocolloids is not necessarily a colloid by this definition, although hydrocolloids are often added to food colloids for functionality or stability. A final distinction that can be made is the availability and use of hydrocolloids as an extracted ingredient, *e.g.* pectin or carrageenan, compared to that same component *in situ* within its source, such as pectin within a whole lemon or carrageenan within its seaweed source. Hydrocolloids are usually thought of as extracted and refined or semirefined food ingredients added to formulated food systems; hence functionality (*i.e.* viscosity, gelation) is also part of the definition. Often they are extracted from by-product streams of food processing (*e.g.* pomace from juice processing, okra from tofu processing, or bran or hulls from cereal and oilseed processing), hence adding value to the commodity. Therefore, it is important to distinguish hydrocolloids from colloids, to recognize which food macromolecules fall into this food ingredient category and why, as well as to understand that there are many overlaps.

Many hydrocolloids are available to the food industry, and as new sources are found from natural products or by-product streams, the list keeps growing. Traditional hydrocolloids are plant-derived ingredients such as pectin, modified starches, modified celluloses, guar gum, locust bean gum, and konjac mannan, along with exudate gums, such as gum arabic, gum ghatti, and tragacanth, and seaweed-derived ingredients, such as agar, alginates, and carrageenan. Gelatin from animal-derived collagen is also a traditional hydrocolloid. Some of these are more familiar in some parts of the world than in others. Newer hydrocolloid ingredients include gums from fermentation, *e.g.* xanthan, gellan, bacterial celluloses, curdlan, or dextran. Cereal β-glucans, arabinoxylans, and xyloglucans are being extracted and modified from hemicellulose to render them as hydrocolloids, and much of that interest is derived from their potential health benefits. Other examples include agricultural by-products such as soluble soybean polysaccharide from okra, flaxseed gum, yellow mustard gum, psyllium, tara gum, fenugreek, and corn fiber gum.

Hydrocolloids are used in foods for two main reasons, either for the physical functionality they add or for their nutritional benefits. Physical functionality is usually either to add viscosity or gelation to a food system. These properties are a manifestation of the chemical structure and conformation of the polymer in solution and in turn are used to deliver functionality such as the development of structure, modification of textural properties of a food system, or shelf-life extension (in which case the term ''stabilizers'' is often used to refer to the hydrocolloid ingredients). Food applications include soups, sauces, gravies, jams, jellies, baked goods, confections, pie fillings, puddings, ice cream, yogurt, foams and emulsions, and many others. Hydrocolloids are also used as edible barrier-layer films

and as encapsulating materials for bioactive compounds. From a nutritional viewpoint, all of the soluble nonstarch polysaccharides and digestion-resistant starch fall into the category of soluble (or viscous) dietary fiber, and this makes up a large component of the hydrocolloid ingredients. These nondigestible carbohydrates can contribute many health benefits, depending on the quantities consumed. Some of the health benefits include reduction in gastroesophageal reflux, enhancement of satiety, reductions in postprandial blood sugar level and LDL cholesterol, and risk reduction of several chronic diseases, including Type II diabetes, obesity, cardiovascular disease, and colorectal cancers.[2–4] Many of the soluble dietary fibers/hydrocolloids are also fermentable, leading to numerous prebiotic functions and enhanced generation of short-chain fatty acids in the colon.[5] Also, some very specific bioactivities are currently being associated with nonstarch polysaccharides.[6] There can also be negative implications from consumption, including mineral binding and hence reduction in mineral absorption, as well as upset in colon functioning leading to irregular stool movement and stool water content and also perhaps enhanced flatulence. Individuals with diseases such as irritable bowel syndrome (IBS) or Crohn's disease need to monitor their intake of nondigestible polysaccharides carefully.

The study and application of food hydrocolloids are a well-developed research and technology area within food science. There are two major biennial conferences on the subject: Gums and Stabilisers for the Food Industry, hosted by the Food Hydrocolloids Trust and held its 20th conference in 2019, and the International Hydrocolloids Conference, approaching its 15th conference in 2020. Proceedings of the Gums and Stabilisers for the Food Industry conferences have been published under the same title after every conference by the Royal Society of Chemistry. A highly recognized journal in the field, *Food Hydrocolloids*, is now at Volume 93 in 2019. Several available textbooks cover this area; some notable titles include Cui,[7] Stephen *et al.*,[8] Biliaderis and Izydorczyk,[6] Morris,[9] Phillips and Williams,[10,11] Imeson,[12] Laaman,[13] and Eliasson.[14] In the remainder of this chapter, we will cover hydrocolloid functionality for structure development in food applications, discuss molecular structure–function relationships, and then present several examples of individual hydrocolloids that contribute unique food functionalities due to particular aspects of their structure (calcium alginate, methylcellulose, high- and low-methoxy pectin, κ-carrageenan, gum Arabic, and xanthan).

1.2 Hydrocolloid Functionality in Food Systems

Hydrocolloids have been extensively used in different food products as thickeners (soups, gravies, salad dressings, sauces, and toppings), water retention agents, stabilizers, emulsifiers, and gel-forming agents (jam, jelly, marmalade, restructured foods, and low-sugar per calorie gels). They also can be applied for inhibiting ice and sugar crystal formation in ice cream and the controlled release of flavors, *etc.* Some of the commonly used hydrocolloids are listed in Table 1.1: *e.g.* modified starch, gelatin, and pectin

Table 1.1 Examples of hydrocolloids used in various food categories.

Food category	Hydrocolloids used
Salad dressing	Xanthan gum, propylene glycol alginate (PGA), modified starch, microcrystalline cellulose (MCC), guar gum
Muscle foods	Modified starch, carrageenan, konjac glucomannan, alginate
Bakery products	Carboxymethyl cellulose (CMC), fenugreek gum, guar gum, konjac gum, xanthan gum
Bakery fillings	Locust bean gum, guar gum, pectin, alginate, PGA, cellulose derivatives, konjac gum, xanthan gum, carrageenan, agar, gellan gum
Frozen dairy desserts	Guar gum, locust bean gum, carrageenan, xanthan gum, alginate, cellulose derivatives, pectin, gelatin
Culture dairy products	Modified starch, locust bean gum, guar gum, gelatin, carrageenan, xanthan gum
Restructured foods	Alginate

can be used in yogurt; xanthan, pectin, and modified starch are used in salad dressing; xanthan and HPMC can be used in whipped topping, *etc.* To understand how the hydrocolloids contribute to the texture, appearance, and mouthfeel of the food products, three main functionalities are discussed further: solubility, viscosity, and gelation.

1.2.1 Solubility

As most hydrocolloids perform their function in aqueous solution, understanding the solubility of polysaccharides is very important, as it allows for the optimization of design and processing conditions of the food products. Application of hydrocolloids in most food products begins by fully dissolving. The dissolution of hydrocolloids is associated with a continuous hydration process, during which the intermolecular binding of the hydrocolloids is gradually converted to molecule–water binding. To achieve the full dissolution of the hydrocolloids, factors including particle size, temperature, and cations all should be considered. For example, compared to a fine powder (particle size higher than 100 mesh), coarse hydrocolloids with a mesh size less than 60 normally take a longer time to dissolve due to the longer time for water penetration. However, hydrocolloids with finer particle sizes may lump together when dissolving due to the formation of so-called fish eyes, *i.e.* particles with a hydrated surface but still undissolved powder in the center. To solve this problem, high agitation mixing and/or premixing with another dry ingredient such as sugar/salt are normally used in industrial applications. Recently, a granulation process has been adopted for hydrocolloid powders that also avoids lumping and helps with quick solubilization.[15] High temperature normally leads to quick dissolution of hydrocolloids; however, a temperature above 80 °C should be avoided for possible degradation of the hydrocolloid molecules. In addition, higher temperature also results in higher energy consumption, leading to increased cost for product manufacturing. Cations also should be considered for the dissolution of some hydrocolloids.

For example, calcium should be avoided for the dissolution of sodium alginate and pectin, as gelation could take place,[13] which prevents the full dispersion of the hydrocolloid molecules in water solution.

Most hydrocolloids are high-molecular-weight polymers and perform their functions as thickeners and stabilizers at concentrations less than 1 wt%. For example, only 0.25% xanthan gum in a pourable French dressing; 0.8% carrageenan in cured hams; 0.7% gums mixture in basic egg pasta. However, some gum-based emulsifiers such as gum arabic require concentrations of even up to 10% to achieve their function. Therefore, understanding the solubility of the gums is critically important for their food application. Different hydrocolloids display distinct solubilities due to their structural and conformational differences; *e.g.* starch is soluble only in hot water, while pullulan and gum arabic are readily dissolved in cold water. Some polysaccharides, such as cellulose, are not water soluble at all, although unmodified cellulose does not technically belong to the family of hydrocolloids. It has been summarized[16] that any structural feature hindering the intermolecular association leads to higher solubility, such as in branching structure or charged groups (carboxylate group, sulfate, or phosphate groups). On the other hand, structural characteristics that promote intermolecular association result in poor solubility, such as in linear chains, large molecular weight, and other regular structural features.

The solubility of some other hydrocolloids is summarized in Table 1.2. Gum arabic for example, has a highly branched molecular structure with excellent water solubility, up to 30% at room temperature, and has been commercially used as an emulsifier. Its detailed structure and functional relationships are discussed further in Section 1.4 of this chapter.

Table 1.2 Solubility of some typical polysaccharides and their structural characteristics. Adapted from ref. 16 [https://www.intechopen.com/books/solubility-of-polysaccharides] under the terms of a CC BY 3.0 license [https://creativecommons.org/licenses/by/3.0/].

Solubility groups	Polysaccharide	Monomer	Special/ charged group	Branching situation	Conformation
Poor solubility	Cellulose	4-β-D-Glc*P*	No	Linear	Ribbon
	Xylan	4-β-D-Xly*P*	No	Linear	Ribbon
	Mannan	4-β-D-Man*P*	No	Linear	Ribbon
Intermediate	Cereal β-glucan	4-β-D-Glc*P*, 3-β-D-Glc*P*	No	Linear	Random coil
	Konjac glucomannan	4-β-D-Glc*P*, 4-β-D-Man*P*	Acetyl group	Linear	Random coil
	Locust bean gum (galactomannan)	4-β-D-Man*P*, T-α-D-Gal*P*	No	Less and short branched	Random coil
Easily soluble	Gum arabic per gum ghatii	3,4,6-, 3,6- Gal*p*, T-Ara*f*, *et al.*	Glucuronic acid	Highly branched	Spherical
	Pullulan	4-α-D-Glc*P*, 6- α-D-Glc*P*	No	Branched	Random coil

1.2.2 Viscosity

As an important functionality, the thickening properties that hydrocolloids contribute in food systems are mainly due to their viscosity. *Viscosity* can be expressed as the ratio of stress to strain (shear rate). Hydrocolloids can impart viscosity to a solution due to intermolecular entanglements, which lead to the resistance to flow under shearing forces.

Viscosity can be characterized by different techniques, some are very simple such as using Bostwick flow methods to determine the flow speed of a fluid food product under gravity down a defined slope for a specific time. However, *apparent viscosity*, which is the shear stress applied to a fluid divided by the shear rate, can be measured using more advanced equipment such viscometers or rheometers, where the shear stress/shear rate can be varied and the relationships between apparent viscosity and shear rate can be used to describe rheological properties. The rheological properties of hydrocolloids can be classified as shear thinning (pseudoplastic), shear thickening (dilatant), or Newtonian flow behavior, in which apparent viscosity is decreased, increased, and constant, respectively, with the applied shear rate (Figure 1.1).

Factors including solvent, temperature, concentration, pH, salt, and molecular structure all can affect the apparent viscosity of hydrocolloid solutions or dispersions. For example, higher temperature normally leads to a decrease in viscosity as it promotes disentanglement of the intermolecular chains. The Arrhenius equation reflects the relationships between apparent viscosity (η) and temperature (T) for solutions with Newtonian flow behavior:

$$\text{Log}\ \eta = \text{Log}\ A + \frac{E}{R}\frac{1}{T} \tag{1.1}$$

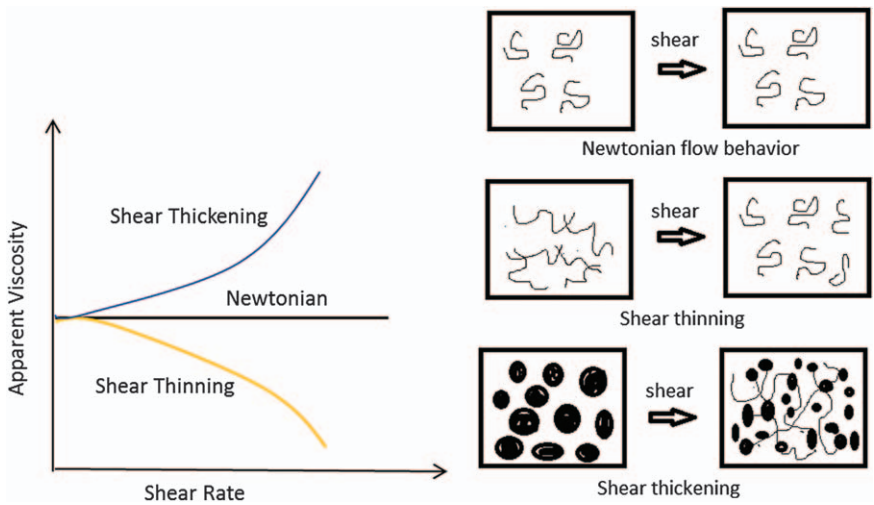

Figure 1.1 Shear flow behaviors of hydrocolloid solutions and the corresponding molecular interactions.

where E is the activation energy for viscous flow, R is the (ideal) gas constant, and A is a constant.

Viscosity is also highly affected by the concentration of the hydrocolloid. For dilute solutions, in which molecular interactions are rare, viscosity increases linearly with concentration but with a low slope. When concentration reaches a specific point where the molecules start to contact/interact with one another (referred to as the *critical concentration* of the hydrocolloid), the viscosity exhibits a step change, beyond which a higher rate of viscosity increase with concentration can be seen (*i.e.* slope increases) due to molecular entanglement, as shown in Figure 1.2.

To compare the viscosity of hydrocolloids in different solvents or under different conditions, intrinsic viscosity (also referred to as inherent viscosity) is generally used. Definitions such as relative viscosity, specific viscosity, and intrinsic viscosity are commonly used with the equations as follows:

$$\eta_{\text{rel}} = \eta_{\text{sol}}/\eta_{\text{solvant}} \tag{1.2}$$

$$\eta_{\text{sp}} = \eta_{\text{rel}} - 1 \tag{1.3}$$

The relationships of specific viscosity (η_{sp}), relative viscosity (η_{rel}), and intrinsic ($[\eta]$) viscosity could be expressed using the Huggins and Kramer equations:[18,19]

$$\eta_{\text{sp}} = [\eta]c + K'[\eta]^2c^2 \tag{1.4}$$

$$\ln(\eta_{\text{rel}}) = [\eta]c + (K' - 0.5)[\eta]^2c^2 \tag{1.5}$$

The intrinsic viscosity $[\eta]$ can be obtained by extrapolating concentration c to zero in either of these equations (Figure 1.2a) and represents molecular volume occupancy (volume per weight, *e.g.* mL g^{-1}). Intrinsic viscosity is proportional to the molecular weight according to the Mark–Houwink equation:[20,21]

$$[\eta] = kM_v^{\alpha} \tag{1.6}$$

The critical concentration (C*) for different hydrocolloids varies and is directly related to their individual intrinsic viscosities. The onset of entanglement for a wide range of neutral and charged polysaccharides is found to occur when $C[\eta] \approx 4$ (*i.e.* $C^* \approx 4/[\eta]$). In other words, the higher the intrinsic viscosity of the polysaccharide, the lower the concentration at which C* is exceeded (Figure 1.2b–d).

As can be seen from Table 1.1, mixtures of hydrocolloids are commonly used to impart improved rheological characteristics to food products, and, if the blend gives rise to synergistic interactions, an added incentive is a reduction in total hydrocolloid concentration and hence costs. Classic examples include galactomannan with xanthan gum or seaweed gum. For example, the synergistic effects of guar gum with xanthan, locust bean gum with xanthan, tara gum with xanthan, and locust bean gum with carrageenan have all been previously reported.[22]

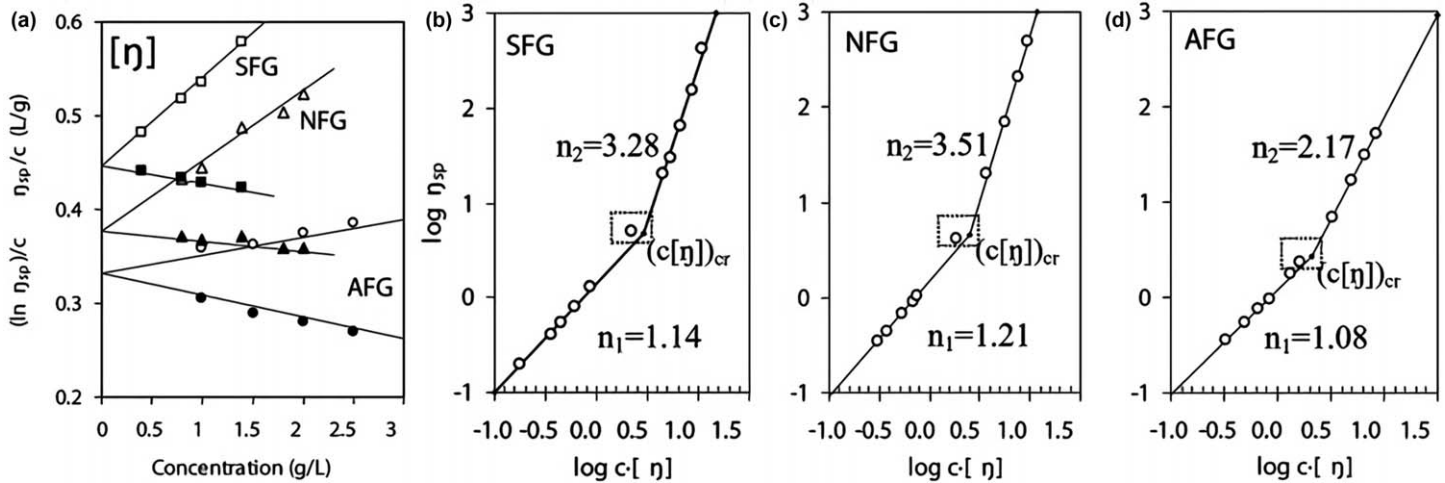

Figure 1.2 The intrinsic viscosity (a) and the dependence of viscosity on concentration (b–d) for three types of flaxseed gum. SFG: soluble flaxseed gum; NFG and AFG: neutral and acidic fraction gum.
Adapted from ref. 17 with permission from Elsevier, Copyright 2012.

1.2.3 Gelation

Specific hydrocolloids can function as gel-forming agents in food products. The most commonly used gel-forming agents include the protein gelatin and the polysaccharides alginate, pectin, carrageenan, gellan, agar, modified starch, methyl cellulose, and hydroxypropyl methylcellulose (Table 1.3). Gel formation is the phenomenon involving the association or cross-linking of the polymer chains to form a three-dimensional network that traps or immobilises the water and other additives such as solutes and pigments within it. The associated regions, known as junction zones, may be formed by two or more polymer chains (Figure 1.3). The gelation process is essentially the formation of these junction zones.[23] The intermolecular interactions that contribute to

Table 1.3 Major hydrocolloid gelling agents and their characteristics. Adapted from ref. 22 with permission from Springer Nature, Copyright 2010.

Hydrocolloid as a gelling agent	Characteristics	Food application
Modified starch	Thermally irreversible opaque gel formed upon cooling	Dairy desserts
Agar	Thermally reversible gel formed upon cooling	Bakery products, jellies
κ-, ι-carrageenan	Thermally reversible gel formed upon cooling	Pudding, milkshakes, tofu
High methoxy pectin	Thermally reversible gel formed upon cooling at low pH	Jams, jellies, glazes, milk-based desserts
Low-methoxy pectin	Thermally reversible gel formed upon cooling at high pH	Low-sugar jams, jellies
Gellan gum	Thermally reversible transparent gel formed upon cooling	Water-based fruit-flavored jellies, lemon jelly
Alginate	Thermally reversible gel that does not melt on heating	Restructured foods, cold-prepared bakery creams
Methyl and hydroxypropylmethyl cellulose	Thermally reversible gel that does not melt on heating	Salad dressings, cake batters, beverages, whipped topping

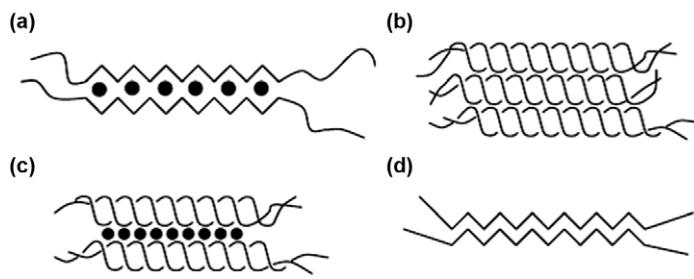

Figure 1.3 Examples of junction zones models for polysaccharides gels: (a) egg box junction, (b) aggregated double helical junction, (c) cation-promoted association of double helices, (d) association of extended ribbon-like structure. Adapted from ref. 24 with permission from Taylor & Francis Group, LLC, Copyright 2005.

junction zone formation include hydrogen bonding, ionic or ion–dipole bonding, van der Waals attraction, and hydrophobic interactions. The physical arrangement of these junction zones within the network can be affected by various parameters such as temperature, the presence of ions, and the inherent structure of the hydrocolloid. It also should be noted that the formation of junction zones by themselves can lead to molecular aggregation and precipitation of hydrocolloids if the zone of interaction is too long. Therefore, a *structure breaker* in the junction zone is also critical for gel formation. The structure breaker is responsible for limiting the length of one junction zone and allowing for the formation of another junction zone elsewhere in the same molecule, with differing molecules (Figure 1.3). This fills the three-dimensional space with the polymer and allows for the trapping and holding of a high degree of water. For example, (1→4)-β-D-glucans interact and lead to the precipitation of the molecules; they are therefore water insoluble and reluctant to form gels. However, mixed-link (1→3)(1→4)-β-D-glucans are somewhat water soluble due to the kinks of β 1→3 linked glycosidic bonds. Xylan structure is water insoluble, while arabinoxylans are water soluble and form gels due to the structure breaker of arabinose as a side chain. Rhamnose ''kinks'' in pectin are also structure breakers.

The junction zones formed by most gelling agents can be disrupted through heating and reformed upon cooling, with such species referred to as thermally reversible gels; however, for some other gelling agents, the molecular interactions are thermally irreversible.

To induce gelation, polysaccharides first need to be well dissolved or dispersed in solution and then exposed to a controlled change in environmental conditions that will lead to the formation of the three-dimensional structure (the junction zone). Gelation can be induced in three ways: ionotropic gelation, cold-set gelation, and heat-set gelation. For ionotropic gelation, the hydrocolloid (mostly negatively charged polysaccharides) could gel in the presence of ions (mostly cations). Typical examples are alginate, carrageenan, and low-methoxy pectin with Ca^{2+}. In cold-set gelation, first hydrocolloid powders are dissolved in warm/boiling water to achieve full dispersion and hydration, then the enthalpically stabilized interchain association can be formed upon cooling, leading to a three-dimensional network. Most of the hydrocolloids form gels by this mechanism; agar and gelatin are two typical examples. For heat-set gelation, hydrocolloids – such as curdlan, konjac glucomannan, methyl cellulose, hydroxypropylmethyl cellulose, starch, and globular proteins – first need to be heated. Heating results in the unfolding of their molecular structures, which are then rearranged into a network.[22] Increases in the temperature of methyl cellulose and hydroxypropylmethyl cellulose solutions will first lead to a minor decrease in viscosity, followed by an eventual sharp increase when the gelling temperature is reached (52 °C for methyl cellulose and 63–80 °C for hydroxypropylmethyl cellulose).

Hydrocolloids as gelling agents have been applied in many food products. For example, agar is used in water dessert gels, aspics, confectionery jellies, canned meats, icings, piping gels, and flan desserts. Agar is extracted from

Table 1.4 Typical water jelly formulation.

Ingredients	Quantity (%)
Sugar	12–15
Agar	0.8–0.85
Color	As required
Flavor	As required
Water or fruit juice	Up to 100

red seaweed (*Rhodophyceae*), is insoluble in cold water, and hydrates when boiled. Cooling an agar solution below 40 °C produces very firm brittle gels. A water jelly formulation is shown in Table 1.4.

1.3 Molecular Structures of Hydrocolloids and Structure–Function Relationship

As discussed in the Introduction, most hydrocolloids are polysaccharides, which are inherently heterogeneous species in terms of chemical structure and molecular weight distribution. The diversity in structural features, such as monosaccharide composition (simple *versus* complex), linkage patterns, chain shapes (linear *versus* branched), functional groups, and conformations, is linked directly to the physical properties of the hydrocolloids, including solubility, rheological properties (viscosity), and gelling properties. It can be generalized that any polysaccharide structure that hinders intermolecular association usually leads to higher solubility, such as branching or charged groups (carboxylate, sulfate, or phosphate groups); on the other hand, structural characteristics that promote intermolecular association result in poor solubility, such as linear chains, large molecular weight, and other regular structural characteristics. In terms of viscosity, normally higher molecular weight and molecules with rigid conformation result in higher viscosity. For gelation, any structure that enhances the formation of junction zones tends to form a gel.

1.3.1 Molecular Weight and Molecular Weight Distribution

Polysaccharides are polydisperse in molecular weight (M_w), which is referred to as molecular weight distribution. Molecular weight and molecular weight distribution play a critical role for the solubility, viscosity, and gelation of polysaccharides. High molecular weight molecules usually have a large excluded volume [eqn (1.7)], which promotes intermolecular interaction of polysaccharides and suppresses solubility.

$$V_h = \frac{[\eta]M}{\gamma N_A} \tag{1.7}$$

where V_h is the hydrodynamic volume, M is molar mass, N_A is Avogadro's number, and γ is Simha's parameter related to the shape of a particle. Almost all carbohydrate polymers with degrees of polymerization (DP) less than 20 are

soluble in water.[25] Solubility decreases with the increase of molecular weight. However, polysaccharides with larger molecular weights normally generate higher viscosities under the same concentration, as such species tend to exhibit intermolecular associations. For example, the viscosity of cellulose gum is determined largely through controlling cellulose chain length or DP.

Molecular weight is also important for gelation. Intermolecular associations of polysaccharides, the prerequisite for gelation to occur, are stable only when the molecular chain length is long enough, typically with a DP value above 20.[24] Normally the gelling ability of the polysaccharides increases with the increase of M_w. The elastic modulus (G′, also referred to as storage modulus, reflecting the strength of the gel) increases with increasing molecular weight up to a certain point (then becoming independent of M_w), whereas rupture strength continues to rise with increasing molecular weight. It is noteworthy that for some neutral polysaccharides such as (1→3)(1→4)-β-D-glucans, lower molecular weight samples form stronger gels than higher molecular weight samples. To some extent, the gelation rate is reported to be inversely proportional to the molecular weight of the polysaccharide. When M_w is above ~500 kD, gel formation is inhibited. The mechanism proposed is as follows: Low-molecular-weight (1→3)(1→4)-β-D-glucans exhibit higher mobility in solution, which increases the probability of interactions between the molecules and hence the formation of ordered structures (junction zones).[24]

1.3.2 Charged and Neutral Polysaccharides

Some polysaccharides carry charged groups (mostly negatively charged, although some are positively charged) onto their molecular structure. The charged groups help with the solubility of polysaccharides in two ways: (1) increasing the molecular affinity to water and (2) preventing intermolecular associations due to the electrostatic effects posed by the charged group.

A relatively higher viscosity could be obtained for charged polysaccharides due to the chain extension caused by the repulsion of the charged group (*e.g.* carboxylic groups) within the molecule. Increasing the ionic strength of the solution could shield these charge effects, thus compromising the extension of the chain and therefore decreasing viscosity. However, when ionic strength reaches a critical value, the viscosity increases again due to the solvent environment change and increase of the intermolecular cross-links as well. Decreasing the pH value normally leads to a viscosity increase with negatively charged polysaccharides due to intermolecular association, and sometimes gel formation could be induced. One typical positively charged polysaccharide is chitosan, which is derived from the deacetylation of chitin. The positively charged groups (from the protonation of free amino groups) are the key to its water solubility. Chitosan is insoluble in basic environments due to the neutralization of the positive charge. However, in acidic environments, protonation of the amino groups increases the degree of water solubility. Due to this property, chitosan has been widely used for drug delivery, *e.g.* the transport of insulin.[16]

1.3.3 Branched and Linear Polysaccharides

Linear polysaccharides with highly regular conformations are mostly insoluble as they can form crystalline or partial crystalline structures due to strong intermolecular associations. Polysaccharides with branching structures demonstrate better solubility because (1) the branching structure could weaken intermolecular association due to steric effects, and (2) molecules with a branched structure exhibit smaller excluded volume and critical concentration, when compared to linear polysaccharides with the same molecular weight. However, in terms of gelling ability, molecules with a high degree of branching are somewhat prevented from forming junction zones and therefore are less likely to form gels.

Taking cellulose as an example, unmodified cellulose is essentially insoluble in aqueous media. Its solubility, however, can be highly increased by decreasing M_w and introducing either charged or branched groups to the molecule. The most commonly used modified celluloses (Figure 1.4) include methyl cellulose (MC), hydroxyl propyl cellulose (HPC), hydroxyl propyl methyl cellulose (HPMC), and carboxy methyl cellulose (CMC). CMC is both cold water and hot water soluble, while MC, HPMC, and HPC can dissolve only in cold water. MC and HPMC form gels with increasing temperature; HPC cannot form a gel while heating; instead, it precipitates when the temperature is increased above 45 °C.

Guar gum and locust bean gum both belong to the galactomannan family. The degree of branching for guar gum (galactose to mannose of 1 : 2) is higher than that of locust bean gum (galactose to mannose of about 1 : 4). In the case of guar, the higher degree of branching prevents the strong cohesion of the main backbones of different neighboring molecules, so that no extensive crystalline regions can be formed. However, locust bean gum is easier to form gels due to its lower degree of branching, which favors the formation of junction zones.

Carrageenans are a family of linear sulfated polysaccharides that are extracted from red edible seaweeds. There are three types of commercial carrageenans, including κ-carrageenan, λ-carrageenan, and ι-carrageenan, which exhibit different structural features as a result of the number and position of sulfate groups in the repeating unit of the polysaccharide (as shown in

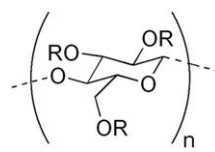

Figure 1.4 Schematic chart for cellulose derivatives: R = H or CH_3 for methyl cellulose; R = H or CH_2COOH for CMC; R = H or CH_3 or $CH_2CH(OH)CH_3$ for HPMC; R = H or $CH_2CH(OH)CH_3$ for HPC.
Adapted from ref. 16 [https://www.intechopen.com/books/solubility-of-polysaccharides] under the terms of a CC BY 3.0 license [https://creativecommons.org/licenses/by/3.0/].

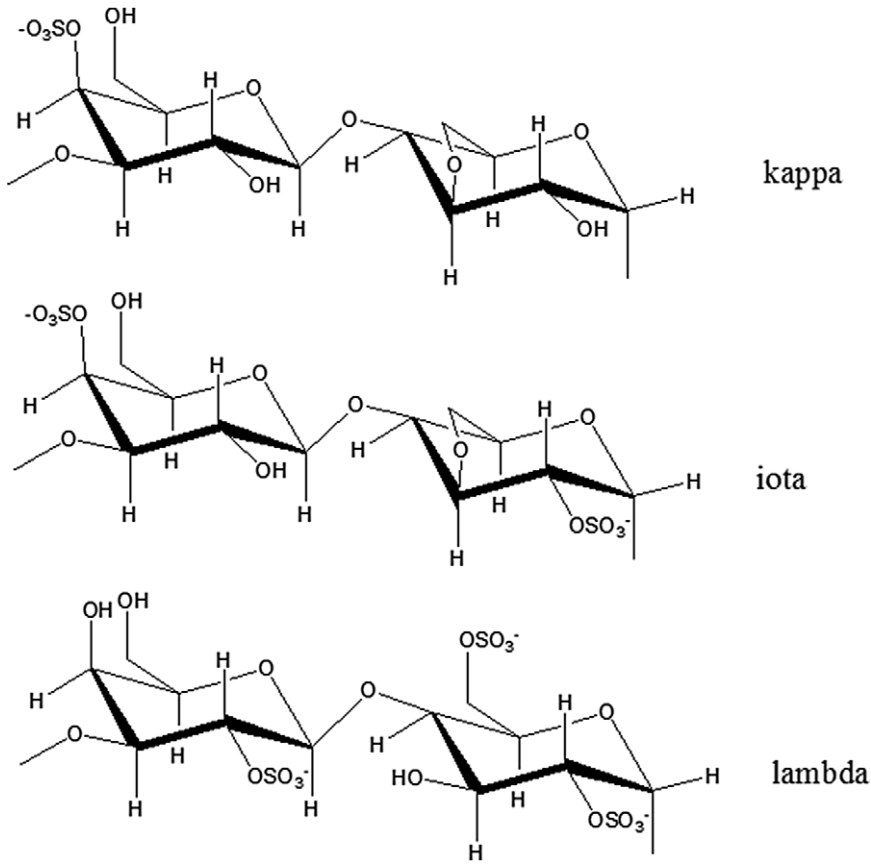

Figure 1.5 Molecular structural comparison for three carrageenan categories.

Figure 1.5). The higher levels of ester sulfate in λ-carrageenan (three sulfate groups per repeating unit) contribute to gel inhibition and result in good water solubility. With the decrease of sulfate groups in the repeating unit, carrageenan starts to form a soft gel (ι-carrageenan, two sulfate groups per repeating unit) and subsequently a rigid gel (κ-carrageenan, one sulfate group per repeating unit).

Starch contains two typical polysaccharides: amylose (mostly linear) and amylopectin (highly branched). During the gelatinization process upon heating, both amylose and amylopectin are released in solution. When cooling, molecules of amylose are much easier to cross-link with each other and form a three-dimensional network than those of amylopectin, which take a much longer time to gel; this process is called *retrogradation*.

1.3.4 Functional Groups

Similar to branching effects, the presence of some hydrophobic groups, *e.g.* *O*-acetyl (*O*-Ac) could also affect the solubility of polysaccharides. *O*-Ac

substituents are present on many cell wall polymers including various hemicelluloses, the pectic polysaccharides, and the polyphenol lignin. For example, xylan, with a degree of acetylation (DA) of 2.0, only dissolves in nonpolar solvents like chloroform or polar aprotic solvents such as dimethyl sulfoxide, while the weakly acetylated xylan (DA ~ 0.5) is totally water soluble, and the nonacetylated xylan (DA ~ 0) is only partially soluble in hot water, due to spontaneous intramolecular hydrogen bonding.[16]

Some other special groups also highly affect the gelation of polysaccharides. For example, arabinoxylan, an important hemicellulose in cereal bran, and psyllium husk can easily form gels in the presence of ferulic acid. The gel-forming ability of arabinoxylan is highly reduced after alkaline treatment, as ferulic acid can be easily removed by alkaline treatment or extraction.[26]

1.3.5 Molecular Conformation

Conformation refers to the way that polymer chains align themselves in solution to adopt an orientation with a lower or the lowest energy. Two general types of conformation for polysaccharides, governed by the regularity of their molecular structure, can be identified: ordered conformation and disordered conformation. In aqueous solution, most of the nonstarch polysaccharides with heterogeneous structure demonstrate disordered conformation, including random coil, rigid, and spherical conformation.

If the values of the torsion angles are fixed by cooperative interactions between sugar residues, such as in solid or gel states, an ordered conformation can be adopted. Two general ordered conformations are the ribbon-like and helix conformations. Polysaccharides with ribbon-like conformation are most easily aligned and closely packed through numerous hydrogen bonds and van der Waals forces. The resultant compact structures essentially prevent solvent penetration and remain insoluble in water. Polysaccharides such as cellulose, xylan, and mannan, which contain the zig-zag types of linkages, all belong to this type. Another ordered conformation is the hollow helix conformation, in which the glycosidic bonds adopt a U-turn form, as in 3-β-D-Glc*P* (curdlan) and 4-α-D-Glc*P* (amylose from starch). Compared to the ribbon-like conformation, the hollow helix conformation has better solubility. Yet this is still not comparable to the solubility of polysaccharides with a disordered conformation (random coil); as an example, amylose, which adopts the helix conformation, is able to dissolve and form a gel in water.

Alginic acid is a copolymer of the building blocks of β-D-mannuronic acid (M) and α-L-guluronic acid (G) linked through 1–4 glycosidic bonds. The molecule contains G-blocks, M-blocks, and MG mixed regions. Due to conformational differences, molecules with a high ratio of G-block regions favor the formation of junction zones in the presence of Ca^{2+}. Therefore, high D-mannuronic acid alginates form turbid gels with low elastic moduli; in contrast, high L-guluronic acid alginates form transparent, stiffer, and more brittle gels. Detailed information regarding the gelation of alginate is provided in Section 1.4 of the present chapter.

In summary, the balance between molecule–molecule interactions and molecule–water interactions is the key to understanding polysaccharide solubility, viscosity, and gelation. In dilute solutions of polysaccharides with low M_w (intrinsic viscosity), the interactions between polysaccharide and water molecules are dominant, leading to low viscosity and normally a Newtonian flow behavior. When hydrocolloids reach the critical concentration or the molecular weight increases (intrinsic viscosity increases), molecules start to interact with one another, viscosity sharply increases, and solutions normally exhibit a pseudoplastic flow behavior. For some specific hydrocolloids with the involvement of ions, temperature change, pH change, or addition of other solutes, the interactions between polymer segments are dominant and could induce gelation when ordered molecular structures, *e.g.* junction zones, are formed. In other words, gelation occurs due to the formation of intra- and intermolecular associations, where hemiacetal oxygen and hydroxyl or methyl groups of the sugar residues of the polysaccharides contribute to hydrogen bonding or van der Waals forces of attraction.[27]

1.4 Unique Examples

As previously discussed, the many and varied molecular structures and interactions among polysaccharides can lead to unique functionalities for very specific applications.[7,8,10,14] In this section, a few of these unique functionalities and applications are presented as examples of the use of hydrocolloids in food structure development.

1.4.1 Sodium/Calcium Alginate

Alginates are structure-forming components in marine brown algae. Alginates are linear, unbranched block copolymers of (1–4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G), distributed as long homopolymeric regions of M-blocks or G-blocks or heteropolymeric MG-, MGG- or MMG-structures, the frequency of which depends highly on source. The guluronate residues are in the $^1C_4$ conformation, while the mannuronate residues have the $^4C_1$ conformation. Since the $^1C_4$ conformation of the guluronate residues makes the glycosidic linkage diaxial in G-blocks, these have a very distinctive ''eggbox'' type of structure (Figure 1.6a). On the other hand, the M-block regions are characterized by diequitorial glycosidic linkages, leading to linear and extended structures (Figure 1.6a). The carboxylic acid group of both mannuronate and guluronate leads to ionized, negative charges at neutral pH, usually bound with Na^+. These two factors taken together are responsible for the strong ionic cross-linking of divalent cations with G-blocks and give rise to the well-known and highly utilized reaction between alginates (specifically the G-block regions) and calcium ions to create strong gels (Figure 1.6b).

The industrial formation of alginate gels is characterized by the control of the ionic cross-linking process. Typically, Ca^{2+} ions are introduced into

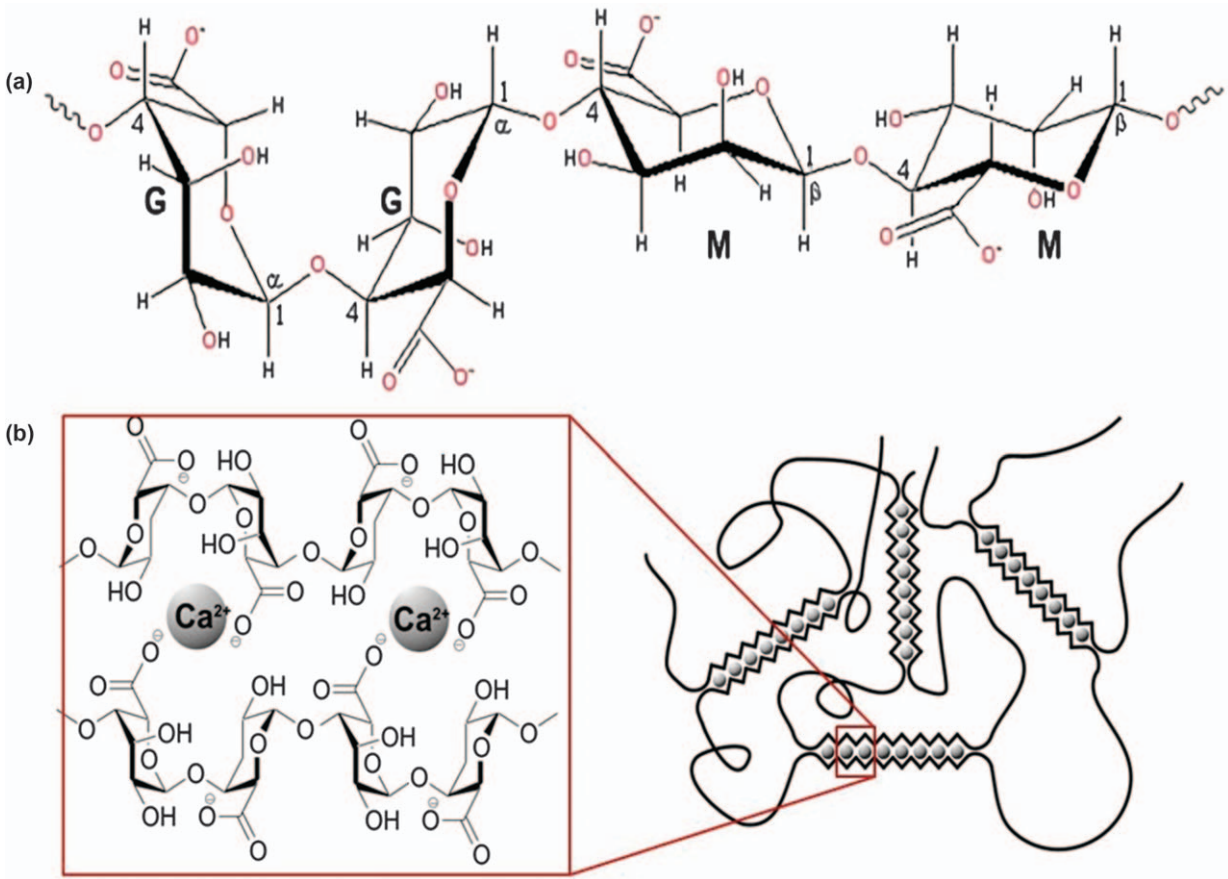

Figure 1.6 The structural units of alginate: (a) G: α-L-guluronic acid; M: (1–4)-linked β-D-mannuronic acid; (b) gel formation of alginate with calcium.
Adapted from ref. 28 with permission from Elsevier, Copyright 2015.

solutions of sodium alginate, where sodium has shielded the charges, and ion exchange occurs, leading to cross-linking of G-block regions (junction zone formation), while M-block regions or heteropolymeric regions act as structure breakers, leading to development of a three-dimensional macromolecular superstructure. The process has to be properly controlled due to the very rapid and irreversible binding reaction. Factors affecting gel formation kinetics and gel strength include the concentration, molecular structure (M : G ratio and distribution), and molecular weight of the alginate molecule being used; the source of the Ca^{2+} ion (chloride, carbonate, *etc.*); and the presence of other modifying factors such as chelators or glucono-σ-lactone (GDL).

The two primary methods for gelation are the diffusion set method and the internal set method. Diffusion setting gives rise to alginate bead or ribbon formation or specifically shaped gel particles. Typically, sodium alginate solution is dripped or streamed through a nozzle into solutions of calcium chloride. Rapid gelling occurs at the surface and diffuses inward as calcium ions exchange with sodium ions, leading to G-block cross-linking. The elasticity of the gel corresponds directly to G-block length. This method of gelation is used to create restructured beaded products like artificial berries, caviar, or gelled beads that can encapsulate other materials for the manufacture of products like fish feed. It is also used for the gelation of pimento strips, often used to stuff pitted olives, and for the formation of onion rings formulated from a slurried preparation of onions. Lately, it has also been used in molecular gastronomy to produce unique culinary dishes.[29]

Restructured foods are a good example to show how gelation is achieved. Restructured foods involve a complex assembly of raw materials and ingredients and a number of texture and structure processes. A restructured food is held together with a gelling system so that it can stand up under its own weight, for which sodium alginate is a good choice. A typical restructuring process consists of three parts:

1. A given raw material is disassembled and cut into smaller pieces of similar size.
2. The disassembled material is reassembled by intimately mixing it with sodium alginate or a solution of sodium alginate.
3. The mixture is then subjected to a treatment with a calcium salt. The reaction normally occurs at ambient temperature and pressure.

Table 1.5 shows a typical formulation for restructured onion rings, for which 1.1% sodium alginate and 3–5% calcium chloride hexahydrate are used.

The internal setting method relies on the slow release of the cross-linking ion. Either calcium carbonate or Ca^{2+} ions complexed in a chelating agent such as EDTA could be used. In either case, the release of Ca^{2+} ions is triggered by a gradual change in pH, often through a slow-release acid such as GDL. Internal set gels can be made in variously shaped molds for unique gel shapes or, once formed, can be further cut into pieces.

Table 1.5 Typical formulation of restructured onion ring. Adapted from ref. 13 with permission form John Wiley & Sons, Copyright © 2011 Blackwell Publishing, Ltd. and Institute of Food Technologists.

Phase	Ingredients	wt%
Alginate/onion	Minced, dehydrated onions	20
	Flour	14
	Salt	0.1
	Sodium alginate	1.1
	Water	64.80
	Total	100
Setting bath	Water	95–97
	Calcium chloride hexahydrate	3–5
	Total	100

1.4.2 High-/Low-methoxyl Pectin

Pectins, extracted for food use from the cell wall middle lamella of fruit waste (*e.g.* apple pomace or citrus peel), are defined as high-molecular-weight heteropolymers containing at least 65% galacturonic acid units, either free or naturally esterified with methanol. In their natural state, pectins also contain various neutral sugars, including rhamnose in the main chain and galactose, arabinose, rhamnose, and others as complex, neutral sugar side chains. The uronic acids and sugars are distributed as linear, unbranched blocks of α-1-4–linked homopolygalacturonan (HG; smooth regions) and as highly branched blocks comprised of rhamnogalacturonans (RG; hairy regions), although many of the side chains will be hydrolyzed under the hot acidic conditions of extraction. In the food industry, pectins are normally used for gelation, which is both pH and sugar-content dependent. A wide range of pectins is commercially available. Extracted pectins are normally 67–73% methyl esterified, referred to as high-methoxyl (HM) pectins, although the degree of esterification (DE) is easily reduced with processing. HM pectins require a high soluble solids (sugar) content and low pH to gel. Pectins with DE ~60% are slow-setting HM pectins, enabling gels to be prepared at higher sugar contents; these are used, for example, in sugar confectionery. Reduction in DE to <50% produces low-methoxyl (LM) pectins, which in terms of gelation are less reliant on soluble solids content and pH but more dependent on the presence of divalent cations (particularly calcium). Since pectins are widely used for food structure formation, and the resulting food microstructures are highly dependent on molecular structure and conformation, the gelation of HM *vs.* LM pectin will be described in more detail as another example of hydrocolloid use in food structuring.

With HM pectins, approximately 65% sugar and pH < 3.4 (rapid-set HM pectin) or 3.2 (slow-set HM pectin) are required for gelation. The most common applications for HM pectins are in fruit jams and jellies. The high solute content achieves a low-water-activity, hydrophobic environment that

minimizes pectin-solvent interactions and promotes pectin–pectin interactions. The H^+ ions (at the low pH conditions) achieve sufficiently low ionization of the unesterified carboxyl groups to minimize electrostatic repulsions (charge neutralization). This results in junction zone formation in the HG regions and disorder in the RG regions, leading to the formation of a supermolecular three-dimensional gel structure.

With LM pectins, gelation is mainly controlled through interactions of unesterified (hence charged) galacturonic acid residues with neighbouring molecules through divalent cations (*e.g.* Ca^{2+}), forming junction zones similar in some respects to the gelation of alginates but perhaps with less well-defined ''eggbox'' cavities. LM pectins can gel over a wide range of sugar content, as low as 10%, and within a wide pH range, >pH 5.0, making them very suitable for low-sugar jam and jellies.

1.4.3 Methyl Cellulose

Cellulose, an insoluble and indigestible β-1-4–linked glucose polymer, can be chemically modified to make a wide range of functional food ingredients through addition of substituent groups to anhydroglucose monomers. The properties and functionality of modified celluloses depend entirely on the type and concentration of the substituent groups. Probably the most common example is carboxymethyl cellulose or cellulose gum, modified to provide water solubility and viscosity. One very unique cellulose derivative is methyl cellulose (MC) or its closely related molecule hydroxypropylmethyl cellulose (HPMC). Formation of MC replaces hydroxyl groups or the hydroxyl of carboxyl groups on the anhydroglucose monomers, with a methyl group (*i.e.* –OH converted to $–OCH_3$, or $–CH_2OH$ converted to $–CH_2OCH_3$). MC and HPMC are both soluble in cold water, implying they will hydrate well during low-temperature mixing of food formulations. However, they will both gel reversibly upon heating to above their gelation temperature (which is dependent on methyl substitution but typically >50 °C for MC and 65–80 °C for HPMC). MC produces firm gels, whereas HPMC (slightly more hydrophilic) produces softer gels. Thermogelation can be explained through dehydration of the polymer at elevated temperatures as a result of weak and reducing attractions between water and unsubstituted hydroxyl groups, followed by hydrophobic interactions between molecules.[30] Gel strength increases with heating time and temperature.

This thermogelation gives rise to the important functionalities of MC and HPMC. They serve well as binding and shape retention agents in hard-to-heat food composites that do not otherwise have good binding properties, *e.g.* reformed soy and plant-based protein products as meat analogues. In addition, they can act as barrier agents to reduce oil uptake in fried food batters, such as in onion rings or chicken nuggets. MC can also be used in bakery fillings, sauces, or other fillings within pastries, where boil-out (loss of filling due to boiling when the composite material is otherwise baked or fried, *e.g.* donut or pot pie fillings) needs to be controlled. In such cases, once thermogelation

occurs, filling loss is minimized. In all of these examples, the texture upon consumption is not greatly affected by the thermogelation since it is reversible by the time the product has cooled for eating or within the mouth, although it does show considerable hysteresis from the heating curve.

1.4.4 Carrageenan (Milk Reactivity)

Carrageenans, as discussed in Section 1.3.3, are linear, negatively charged, sulfated ($-SO_3^-$) galactan polysaccharides with differing degrees of sulfation and 3,6-anhydrogalactose content (Figure 1.5). These polysaccharides are similar in backbone structure to agarose, although the latter is neutral and nonsulfated. This differing composition translates into varying functionality. κ- and ι-carrageenans are able to form gels, whereas λ-carrageenan cannot. One of the unique functionalities of κ-carrageenan specifically is its so-called milk reactivity, referring to its interaction with casein micelles, specifically κ-casein, in dairy systems. One aspect of this milk reactivity of κ-carrageenan in nongelled systems is its ability to inhibit visual phase separation between casein micelles and polysaccharides, which occurs readily due to biopolymer incompatibility. Because of the light-scattering effect of casein micelles, phase separation leads to a clear, watery, casein-depleted serum layer forming either above or below (depending on fat content and density) the decreasing-volume protein phase, which is white due to the presence of the casein micelles. Polysaccharide stabilizers often need to be added to dairy products for enhanced product functionality or shelf life. All that is required to stabilize a 4% milk protein per 0.14% locust bean gum system (typical of soft serve ice cream mix) from phase separating is 0.015–0.02% κ-carrageenan, and no other hydrocolloid has demonstrated similar functionality. Since this is a very specific, unique, and highly industrially relevant reaction, owing to the molecular structures and conformations of the two molecules involved and their interactions, it will be described in detail here as another example of hydrocolloids in food structure development.

There are two potential interactions by which κ-carrageenan could stabilize casein micelle systems containing hydrocolloids. The first proposes that the negatively charged κ-carrageenan interacts with a positively charged region of κ-casein (residues 97–112), thus adsorbing to the surface of the casein micelle. However, the surface of the micelle is overall negatively charged and stabilized sterically by the caseino-macropeptide portion of κ-casein (residues 106–169), the so-called hairy layer, which protrudes approximately 5 nm out from the micelle. Thus, for both steric and electrostatic reasons, the prevention of phase separation by direct absorption of κ-carrageenan to the micellar surface seems highly improbable. The second concept therefore proposes that phase separation is prevented *via* the formation of a weak κ-carrageenan gel, which holds the casein micelles suspended, even though concentrations of κ-carrageenan required for stability are below its critical gelling concentration.[31–33]

At elevated temperatures (>50 °C, depending on salt concentration), κ-carrageenan exists in solution as a random coil. However, when the

temperature is sufficiently lowered, the polymer undergoes a transition from a coil to a helix, and κ-carrageenan gelation occurs as a result of helical aggregation. Ions also play a vital role in the formation of the κ-carrageenan helix and gelation. Cations, such as potassium and calcium, affect the transition temperature as well as aiding in helical aggregation, and certain anions, such as iodide, affect gelation by interacting with the helix and inhibiting helical aggregation, thus preventing gel formation. Within the ionic environment of milk (10.2 mM calcium and 33.3 mM potassium), κ-carrageenan is in an environment favorable for gelation, provided the polymer concentration is high enough.

Research work performed in the authors' laboratory suggests that both κ-carrageenan adsorption to casein micelle surfaces and κ-carrageenan helix–helix aggregation are required for the polymer to be effective in preventing casein micelle macroscopic phase separation from polysaccharides.[31–33] Electron microscopy and light scattering data suggest that κ-carrageenan in the helix form interacts with the surface of the casein micelle, perhaps because of its degree of sulfation and increase in charge density when in the helical form. Light and confocal microscopy showed that carrageenan-containing systems that did not exhibit visual phase separation were nevertheless phased-separated into water-in-water-type emulsions at the microscopic level. Phase separation experiments in 13% milk solids (not-fat), 0.14% locust bean gum mixed systems with κ-carrageenan in the coil state (>60 °C), κ-carrageenan in the helical state but with helix aggregation blocked (addition of NaI), λ-carrageenan, guar (all at 0.01–0.03%) and agarose (0.01–0.05%) were used to understand the conditions at which stabilization of phase separation occurred. The phase separation experiments suggest that the interaction between casein micelles and κ-carrageenan is not sufficient (by itself) to prevent macroscopic phase separation. By blocking helix aggregation, the stabilizing ability of the κ-carrageenan was reduced. In addition, to support the NaI experiments, replacing κ-carrageenan with nongelling λ-carrageenan resulted in visual phase separation even though the latter also adsorbs to the casein micelle. Conversely, agarose did not adsorb to the casein micelle, nor did it inhibit phase separation, but it did form a weak gel. Thus, this research suggested that both κ-carrageenan–casein micelle interaction and κ-carrageenan helix aggregation are required to prevent casein micelle–polysaccharide macroscopic phase separation and provide visual stability. Based on these results, it is believed that κ-carrageenan functions at the periphery of microscopically phase-separated discrete domains of casein micelles, stabilizing these (microdomains) and preventing them from coalescing and forming visual protein-enriched and protein-depleted phases.

1.4.5 Gum Arabic

Gum arabic is a good example of the use of a hydrocolloid as an emulsifying agent. Its specific use in this regard is for stabilization of flavor (citrus or cola) oil emulsions for carbonated beverage applications, since it is stable in

acidic conditions, and protein emulsifiers typically are not. The polymer is able to inhibit flocculation and coalescence of oil droplets in both the concentrated flavor oil emulsion and in the diluted carbonated beverage over many months, giving it unique stabilizing properties for this application. This structuring property is again owing to its molecular structure and conformation.

Gum arabic is an exudate gum from *Acacia senegal* or *Acacia seyal trees* from Sudan, Nigeria, and Chad. The gum contains two main fractions, arabinogalactan (AG) and arabinogalactan protein (AGP), and it is the protein component that is the key to its emulsifying properties. The polysaccharide component of both fractions is comprised of a β-1-3–linked D-galactose backbone with extensive branching of mostly arabinose, galactose, and some rhamnose and glucuronic acid (~15%).[34] AG takes on the conformation of a thin disk-like structure. AGP has a protein content of ~10%, and its backbone is a polypeptide chain of ~250 amino acids. The AG-like polysaccharide disks of the AGP molecule, with a molecular weight of ~40 000 each, are attached to this protein backbone (Figure 1.7). The entire structure takes on a very compact spherical conformation. Therefore, solutions of gum arabic are very low in viscosity; a 30% gum arabic solution has a viscosity of ~300 mPa s, which is less than that of a 1% sodium carboxymethyl cellulose solution. When used for emulsification, the protein backbone is thought to adsorb to the interface of the oil droplet while the polysaccharide disks stick out into the aqueous phase, providing stability through both steric and electrostatic repulsion (from the glucuronic acids). Emulsification is achieved at fairly high gum arabic concentration due to the low protein content; for example, ~12% gum arabic is required to stabilize a 20% oil emulsion. However, the high surface coating of the oil droplet by the hydrophilic polysaccharide disks gives rise to a very stable emulsion microstructure. While some other gums have shown to provide a reduction in interfacial tension, this is usually associated with some coextracted protein content. However, in the case of gum arabic, the protein is covalently linked to the polysaccharide, making it unique and giving rise to its exceptional food structuring ability.

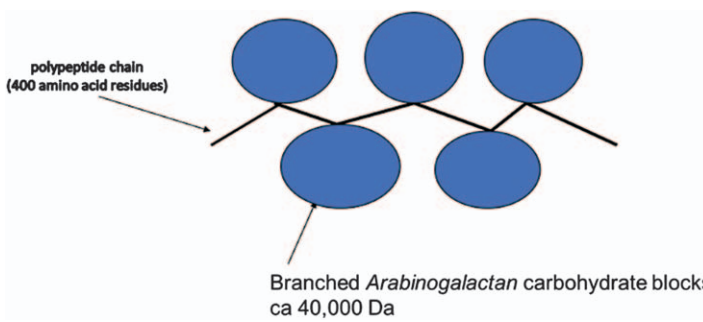

Figure 1.7 Schematic illustration of the Wattle blossom model of gum arabic.

1.4.6 Xanthan

A final example of connecting molecular structure closely to functionality and food structure is the high degree of pseudoplasticity exhibited by xanthan gum. Xanthan is a bacterial polysaccharide consisting of a cellulose backbone substituted at C-3 on alternating anhydroglucose units with a trisaccharide side chain containing two mannose units and a glucuronic acid unit, although there are several substituents on all three side chain residues. The molecular conformation is what gives xanthan its unique properties. It shows a fivefold right-handed helix such that the trisaccharide chains are aligned with the cellulosic backbone and stabilize it primarily through hydrogen bonding. This gives the molecule the structure of a rigid rod when in solution.[35] As a result, xanthan demonstrates high viscosity at low shear rates, low concentrations, and a high degree of pseudoplasticity and thixotropy. A 0.5% xanthan gum solution can exhibit a reduction of 4–5 log cycles in viscosity within a range of shear rates from 10^{-2} to 10^{3} s^{-1}. Xanthan solutions can appear almost gel-like but pour readily, thus providing long-term stability to colloidal systems. A common and demonstrable application is in salad dressings, where its unique functionality gives rise to the ability to be shaken and poured easily but show high holdup on the salad. It can also inhibit sedimentation of particulates in many low-viscosity fluids. The viscosity of xanthan solutions is stable over a wide temperature and pH range. Simplistically, it may be considered that the initially entangled rigid xanthan rods are encouraged to progressively align under the applied shear fields, which gives rise to such rapid drops in viscosity with increasing shear rates. However, the association between molecular structure and solution rheology may be more complex, in that xanthan dispersions have been shown to contain weakly associated microgels or xanthan aggregates due to incomplete conformational ordering of helical sequences,[36] and these aggregates may give rise to a dispersion more akin to a weak gel when at rest.

1.5 Conclusions and Future Perspectives

Hydrocolloids have been important food structuring agents for many years in many traditional foods, such as jellies and pies, and continue to play important and vital roles in novel food structure development, such as in films and encapsulants. The three most important hydrocolloid functional properties are solubility, viscosity, and gelation, which result from their molecular structures and conformations in solution, as was demonstrated in Section 1.3. It is very often the unique molecular structures of specific hydrocolloids that give rise to very specific food applications, as has been demonstrated in Section 1.4.

One of the big challenges for the use of hydrocolloids in today's food and consumer environment is the demand for natural, clean-label ingredients. While most of the hydrocolloids presently in use are from a natural stock,

many of them are extracted or modified by industrial means that do not meet clean-label perceptions. Future developments in this area will likely produce an expanded array of hydrocolloid food ingredients, either from new and novel, untapped sources, many of these from agricultural by-product streams or from process modifications of existing products to render them more natural and/or environmentally friendly. Considerations for future hydrocolloid ingredients will include functionality, cost, and human safety, as has always been the case, but in addition the source and supply, including its carbon footprint, environmental impact, and ''naturalness,'' will be increasingly scrutinized by discerning customers who want to know where their food comes from and how it is processed.

It is also worth noting that most nonstarch polysaccharide hydrocolloids are also dietary fibers, and a great deal of new interest and knowledge surrounds the bioactivity and health-promoting properties of dietary fiber. It is well recognized that most diets in the developed world do not contain enough specific fibers to obtain their full potential, so fiber-fortified foods are increasingly being developed and sought after. Ideal specific hydrocolloids will deliver both biological and physical functionality to food systems for appropriate structure development – enough of one without compromising the other.

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