1
General Overview of Food Hydrocolloids

1.1
Introduction to the World of Hydrocolloids

The term 'hydrocolloid' is derived from the Greek *hydro* 'water' and *kolla* 'glue'.

Hydrocolloids are colloidal substances with an affinity for water. From a chemical point of view, they are macromolecular hydrophilic substances. Some of them are water soluble and form colloidal solutions others are only able to swell in water and can be dispersed by means of shear forces. Hydrocolloids produce viscous solutions, pseudo-gels, or gels in water. The heterogeneous group consists of polysaccharides and proteins.

Hydrocolloids are used in technical and regulated applications to thicken and to stabilize formulations. In processed foods, they are ubiquitous – no other group of ingredients contributes more to viscosity, texture, and body like hydrocolloids do.

Hydrocolloids are not really emulsifiers because, mostly, they do not have the characteristic linkage of lipophilic and hydrophilic groups in the molecular structure. The molecules are too big and complex in size and therefore are not flexible enough to cover the interfaces being formed during homogenization of oil–water mixtures fast enough to create a long-term stable emulsion with sufficiently small droplet diameter. However, these thickeners can stabilize emulsions by increasing the viscosity of the water surface or by interaction with surface-active substances. Some hydrocolloids like gum Arabic or non-ionic products such as methylcellulose (MC), HPMC (hydroxypropylcellulose), or propylene glycol alginate (PGA) reduce the surface tension and exhibit limited emulsifying properties [1].

In accordance to their origin and way of manufacturing, hydrocolloids can be classified in four different groups:

1) hydrocolloids purely isolated from plants (without chemical modification);
2) hydrocolloids obtained by fermentation;
3) plant-derived hydrocolloids that are chemically modified;
4) hydrocolloids from animals.

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Tanja Wüstenberg.

According to their botanical origin and their function in the plant organism, naturally occurring vegetable hydrocolloids can be divided into [1]:

- exudates (protective colloids being deposited on wounds):
  acacia gum/gum Arabic, tragacanth, karaya gum, ghatti gum;
- seed flours (reserve polysaccharides):
  guar gum, locust bean gum, tara gum, tamarind seed gum;
- extracts from land plants and marine algae (scaffolding substances):
  pectins, agar, alginate, carrageenan, starches, cellulose, furcelleran, larch gum.

Additionally, there are [1]:

- microbial or bacterial polysaccharides:
  xanthan, dextran, curdlan, scleroglucan, gellan, pullulan;
- modified polysaccharides:
  propylene glycol alginate, amidated pectin, modified starches, cellulose derivatives;
- proteins of animal origin:
  gelatine, caseinates.

Figure 1.1 presents an overview of globally used food hydrocolloids. There are also other substances available and in use, but several of them are restricted to local use and, depending on availability and legislation, are not in industrially-produced applications. Please always check the relevant legislation before using one of these stabilizers, gelling agents, or thickeners.

The individual substances are described in subsequent sections. Information on their origin, manufacturing, structure, properties, and handling are provided. For the most used products there are overview tables; Tables 1.1–1.9 below give a quick orientation.

The individual cellulose-based substances are then described in more detail. Overview tables for selected cellulose derivatives are given in Section 1.6 (Tables 1.10–1.14).

1.2 Plant Extracts

1.2.1 Agar

Raw Material, Harvesting, and Manufacturing

Agar is a structure-building component of the cell wall of red algae (Rhodophyceae). *Gelidium*, *Gracilaria*, and *Pterocladia* species especially serve as a source of raw materials. The main producing countries are Japan, United States of

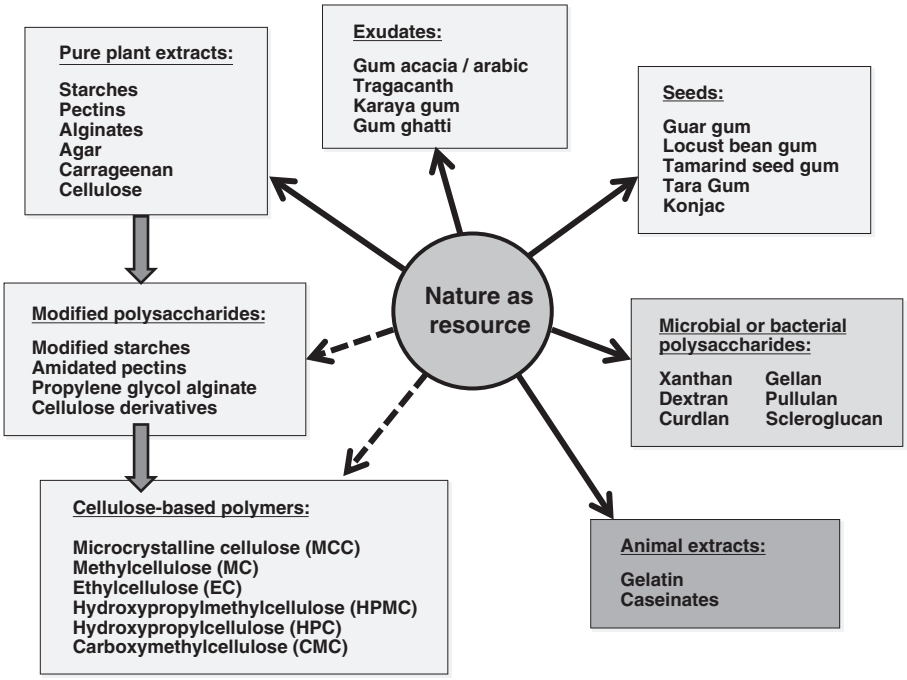

Figure 1.1 Overview of food hydrocolloids used globally.

America (California), Chile, and Spain, on whose rocky shores they occur. Agar was discovered in 1658 in Japan.

The red algae are harvested and extracted under pressure with hot water (100–130 °C (212–266 °F)) at pH 5–6. The extract is purified by filtration or centrifugation and subsequently bleached with calcium hypochlorite. To isolate the agar, the extract is frozen and, after thawing, the remaining gelatinous residue is dried. More recently, the water is squeezed out by means of a high-pressure press, and the remaining water is removed by drying. The annual production involves about 55 000 MT of dried seaweed to manufacture 7500 MT of agar [1,2].

Chemical Structure

Agar is a heterogeneous polysaccharide composed of the monomeric substances D-galactose and (3 → 6)-anhydro-L-galactose (Table 1.1). The main component, which is responsible for the strong gelling ability, is so-called agarose. Additionally, a small amount of a slightly acidic polysaccharide, the non- or only weakly gelling agaropectin, is present. Agaropectin also contains sulfate ester, glucuronic, and pyruvic acid groups. Agarose is a neutral, linear galactan. The D-galactose and 3,6-anhydro-L-galactose monomers are linked alternately by α-(1 → 3)- and β-(1 → 4) bonds with each other. Owing to the high anhydrogalactose portion and the absence of sulfate ester groups, which strengthen the hydrophobic character, agar is a good gelling agent that is independent of cations [1].

Table 1.1 Characteristics of agar.

	Agar
E-No.	E 406
Origin	Seaweed extract
Chemical composition	• Galactose and anhydro-galactose; • low sulfate content (<4.5%, mostly 1.5–2.5%)
Nutritional value (in 100 g) – metabolism	1425 kJ (340 kcal); slow resorption
Fibre content	2.2% (42% protein, 36% carbohydrates)
Toxicology	No health concerns, consumption generally 1–2 g per day (mild laxative effect at 6 g per day); no ADI value defined; considered as food in Asia, not as additive
Solubility at low temperature (H_2O)	Insoluble
Appearance of an aqueous solution	Opaque, yellowish
Viscosity of solution in water	Low, insoluble in cold water
Impact of heat on viscosity in water (pH 7)	Soluble at $T > 80\,°C$ (176 °F)
Viscosity development in water at pH 7 ($T = 0$–$100\,°C$)	Forms a thermoreversible gel after dissolution and cooling to 35 °C (95 °F) (gel melts at $T > 85\,°C$ (185 °F))
Shear stability	High
Thickening effect	High (gel formation)
pH stability	Medium, hydrolysis by cooking in acidic system
Decomposition	Combination of heat + low pH (below pH 4)
Film formation	High
Emulsion stabilization	No
Gelation	Thermoreversible gelation after heating to $T > 80\,°C$ (176 °F) and cooling to 35 °C (95 °F); also gels in saturated sugar solutions; gelation temperature is independent of sugar concentration
Gel strength and gel stability	High gel strength, gels are highly heat-stable
Gel transparency	Low
Tendency for gel synaeresis	High
Impact of electrolytes (cations +, 2+, 3+)	No
Reaction with Ca^{2+} ions	No
Protein activity	Low/no
Crystallization control	No
Synergistic effects with other hydrocolloids	+ LBG or guar: less synaeresis, more elasticity; + 10% LBG: maximum gel strength (+8%); + 10% konjac: maximum gel strength
Other synergistic effects	Enhanced gel strength with high sugar concentrations (>60%) for some agar types
Negative interactions	• Tannic acid can inhibit the gelling process; • gum karaya reduces gel strength of agar gels; • proton scavengers like potassium iodide, urea, guanidine, sodium thiocyanate, and so on block the gelling process and prevent agarose gel formation
Dosage level in foods	Low, typical 0.5–2%, gelation already at 0.2%

Gelation of agarose from aqueous solutions is assumed to occur because of the association of the molecular chains into double helices, which then aggregate to form a network capable of immobilizing the water [3].

The sulfate content of agar is below 4.5% (mostly between 1.5–2.5%) which is very low compared to that of carrageenans [2].

Solubility, Viscosity, and Gelation

Agar is insoluble in cold water. Complete dissolution occurs at temperatures above 80 °C (176 °F). Upon cooling to 30–40 °C (86–104 °F), a thermoreversible gel is formed that melts again when heating above 76–92 °C (169–197 °F), depending on seaweed species and methyl ester content. This transition occurs at higher temperature with increasing agar concentration and decreasing cooling rate. Another vey important property of agar is gel hysteresis – the difference between the gelling and the melting temperature – which is around 50–60 °C (90–108 °F). This hysteresis of agar types with low ester content is much larger than for many other gelling agents (e.g. κ-carrageenan with 15–20 °C (27–36 °F)). Agar is a neutral hydrocolloid whose solubility and gelation is not affected by the addition or presence of electrolytes. Agar does not require cations to gel. The agar gelation process is totally reversible. The gel melts on heating and resets on cooling. This cycle can be repeated many times without significant change in the mechanical properties of the gel, provided the agar is not used at very low pH conditions (<4) or with oxidizing agents. Agar consists of a macromolecular network of agarose molecules associated through hydrogen bonds. Consequently, the presence of proton scavengers such as potassium iodide, urea, guanidine, or sodium thiocyanate block the gelling process by impeding the formation of hydrogen bonds and hence prevent agarose gel formation. Moreover, agar is resistant against enzymes used in food technology [2].

Properties

The ability to form reversible gels by simply cooling hot, aqueous solutions is the most important property of agar. The greatest advantages for agar in different food applications derive from the characteristic firm texture and heat tolerance of the gels, stability under acidic conditions, high solubility in concentrated sugar solutions, and limited reactivity with other food components. Agar can be hydrolysed by acid at high temperature, so for pH values below 5 it is recommended to lower the pH just before cooling to form the gel. The level of use is low and typically between 0.5% and 2%. The threshold for gelation is 0.2%. With locust bean gum (LBG) or guar gum, agar gels exhibit less synaeresis and more elasticity. The maximum gel strength (+8%) of agar is obtained with 10% LBG galactomannan or 10% konjac glucomannan in the mixture. Gel strength is enhanced by high sugar concentrations (>60%). Gum karaya reduces agar gel strength. The presence of tannic acid or pentadiagaloyl glucose found in fruits like quince, apples, and plums can inhibit the gelling process because of their function as proton scavenger. This effect can be overcome by adding low levels of glycerol [2].

Applications

Agar is used in canned meat, fish, and poultry products. It is suitable for use in water- and milk-based desserts, any kind of aspics, and artificial caviar. Sugar-based coatings, glazes, and icings can be formulated with low to high sugar concentrations and are never sticky. Agar is added to confectionary, including jelly beans, nougat, candy fillings, piping gels, jams, and jellies. It acts as texture stabilizer in ice cream and as fining agent to clarify wine, juice, and vinegar. Besides food, it is used in microbiology in high volumes for the preparation of culture media.

Toxicology and Regulatory Affairs

Since time immemorial, seaweed serves the people as part of its food. Long-term experiences in using agar in animal nutrition and clinical results in using as laxative are available. Extensive toxicological studies did not justify any health concerns. Agar has GRAS (generally recognized as safe) status from US FDA. No ADI (allowable daily intake) value has been defined. In Europe, agar is approved as food additive with unrestricted dosage ('quantum saris') and classified as E 406. In Asia it is has been considered to be a food ingredient, not an additive, for centuries with an estimated daily consumption of 1–2 g. The formed gels slowly pass through the stomach, increasing satiety by increasing the feeling of fullness. The increased viscosity moderates glucose and fat uptake and controls cholesterol.

1.2.2
Alginates and PGA

Raw Material Origin, Harvesting, and Quality

Alginate was first described in 1881. The name is now used as the general term for the range of alginic acid salts that can be applied in foods. Alginate occurs in the cell walls and intercellular spaces of brown algae (Phaeophyceae). The alginate molecules provide both flexibility and strength to the plants adapted to the special conditions in the sea. Main sources of raw material are species of *Macrocystis*, *Laminaria*, *Lessonia*, *Eklonia*, *Ascophyllum*, and *Durvillaea*. Brown algae need clean water at 4–18 °C (39–64 °F) and sunlight to produce alginate by photosynthesis.

Alginic acid is extracted directly from brown seaweed through a long and slow process. This is the free acid form of alginate and the water-insoluble intermediate in the commercial manufacture of alginates. The concentration of alginic acid in seaweed is about 15–40% of the dry matter. To produce alginic acid from, for example, *Macrocystis* species the seaweed is cleaned, shredded, and washed after harvesting. The wet or dried algae are extracted by alkaline treatment. The extracts are purified by filtration and the alginic acid is isolated by precipitation with calcium ions or mineral acid. Subsequently, the partially soluble alginic acid is converted into water-soluble alginate products (an exception is Ca alginate) by neutralization with alkali and incorporation of different inorganic

salts ($NaCO_3$, K_2CO_3, NH_4CO_3, $CaCO_3$,). Propylene glycol alginate (PGA) is produced by adding propylene oxide under pressure to a partially neutralized alginic acid. The resulting products are dried and milled. The global annual production of alginate is estimated to be 38 000 MT [1,2].

Chemical Structure

Alginate is a family of unbranched binary copolymers of (1 → 4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues of widely varying composition and sequential structure (Table 1.2). Alginates are salts of alginic acid, a linear polyuronide, with the cations of Na, K, NH_4, or Ca. Depending on the type of algae, the alginic acid is composed of mannuronic acid and guluronic acid in ratios of M : G = 0.4–1.9 : 1. In addition to alternating polymers (M-G-M-G), block polymers also occur in the alginate macromolecule and are constructed only of mannuronic acid (M-M-M-M) or guluronic acid (G-G-G-G). In the pure GGGG- or MM-blocks there is a kind of folded structure, which has an essential role in gelation. In particular, the GG-blocks form a regular zigzag structure. The degree of polymerization for commercial products is in the range 50–3000, corresponding to molecular weights of 10–600 kDa. Propylene glycol alginate is an ester of alginic acid whose uronic acid units are partially (40–85%) esterified with propylene glycol. The remaining carboxyl groups occur partially in free form and partially as sodium salt. The average molecular weight is between 32 and 200 kDa [1–3].

Solubility, Viscosity, and Gelation

Alginic acid and calcium alginate are insoluble in water, while the alkali metal (sodium, potassium) and ammonium salts are easily soluble. Propylene glycol alginate is water-soluble down to pH 2.5, with stable solutions in the range pH 2.5–8. Typically, the alginate powder is dry-blended with particles, such as sugar, or suspended in a hydrophobic solvent, for example vegetable oil to prevent lump formation. The dissolution rate depends on shear force, ionic level with respect to water hardness and solvent temperature. Viscosity in water is correlated to the molecular lengths of the alginate molecules, but is also several influenced by ions present, sugar, polyols, and alcohols. Aqueous solutions have a high viscosity, even at low concentrations, and are very stable when heated in a neutral pH range. In acidic systems at pH <5, the viscosity decreases strongly. Calcium ions greatly increase the viscosity and lead to gelation by incorporation in the zigzag structure of the GG-blocks (egg-box model), which then form three-dimensional networks with other blocks. MM-blocks and MG-blocks will not participate in the junction zones but form so-called elastic segments in the gel network. Viscous solutions of alginate exhibit shear-thinning properties caused by parallel arrangement of the linear molecule chains. Alginate solutions (1–2%) form irreversible gels in the presence of Ca^{2+} ions at room temperature. The gel strength depends on the amount of MM- or GG-block polymers, which cause different bonds. Owing to the high sensitivity to calcium and acids, buffers and sequestrants,

Table 1.2 Characteristics of alginates and PGA.

	Alginates and PGA
E-No.	E 400–E 405
Origin	Seaweed extract/alginic acid derivatives
Chemical composition	• Salt of a linear polyuronide with cations (Na, K, NH_4, Ca); • mannuronic acid (M), guluronic acid (G) (ratio M : G = 4–19 : 10)
Nutritional value (in 100 g) – metabolism	0 kJ (0 kcal); no resorption
Fibre content	100% soluble fibre
Toxicology	No health concerns for salts of alginic acid (therefore no ADI for E 400–404); considered as food in Asia, not as additive; but ADI for PGA (25 mg kg^{-1} BW per day)
Solubility at low temperature (H_2O)	100% Soluble (except for pure alginic acid and calcium alginate)
Appearance of an aqueous solution	Opaque, yellowish
Viscosity of solution in water	High (low for alginic acid and calcium alginate)
Impact of heat on viscosity in water (pH 7)	Heat-stable gels
Viscosity development in water at pH 7 (T = 0–100 °C)	• Ca^{2+}-free: high-viscosity solution; • gel formation in presence of calcium
Shear stability	Pseudoplastic (shear-thinning)
Thickening effect	High
pH stability	Medium (pH 5–9)
Decomposition	• Acid (pH < 5) and alkaline (pH > 9) conditions; • oxidation by free radicals; • enzymes
Film formation	High
Emulsion stabilization	High
Gelation	Cold formation of thermo-irreversible gels by acid and multivalent cations (except magnesium)
Gel strength and gel stability	High strength + high stability during cooking, baking, cooling, freezing
Gel transparency	Low
Tendency for gel synaeresis	Medium
Impact of electrolytes (cations +, 2+, 3+)	High
Reaction with Ca^{2+} ions	Gel formation
Protein activity	Low/no
Crystallization control	Freeze–thaw stable gels possible
Synergistic effects with other hydrocolloids	• Gum karaya: interactions with sodium alginate (modified solutions properties); • HM pectin: strong thermoreversible gels are formed at low solid levels over a wide pH range
Other synergistic effects	—
Negative interactions	—
Dosage level in foods	Medium (typical 0.7–2%)

which slowly release calcium and hydrogen ions, are necessary for the preparation of gels. Suitable substances are slightly soluble calcium salts, polyphosphates, and glucono-δ-lactone [2].

Properties

The most important property of alginates is the ability to form heat-stable gels by cold processing in presence of acids and all multivalent cations except magnesium. Calcium is the most often used gelling cation. Gel formation is controlled by controlling the release of calcium or acid into an alginate solution. Both acid and calcium alginate gels are thermo-irreversible and will form over a wide temperature range. A thermoreversible gel can be made under acidic conditions below pH 4.0, preferably around pH 3.4, by using a combination of alginate and HM pectin. In general, alginate gels exhibit synaeresis over storage time. Synergistic effects of alginates with other hydrocolloids are rare. There are interactions between gum karaya and sodium alginate (modified solutions properties). Alginate forms strong thermoreversible gels with HM pectin at low solid levels over a wide pH range [2].

Applications

In the food industry, alginates are used as emulsifiers, gelling agents, coating agents, and thickeners – and also for organic products. They are applied in diet and light products, baked goods, frozen foods, mayonnaise, salad dressings, dessert jellies, ice cream, mousses, foams, processed cheese, in meat and canned vegetables, and soups. The gums are suitable for encapsulation of prebiotics, flavours, and functional food oil. Alginates are also often used in so-called molecular gastronomy for the production of fish eggs and caviar imitations or in artificial mozzarella. In Asia, bird's nests or shark fins are made of it.

PGA has lipophilic and hydrophilic groups in the molecules and therefore combines the properties of a real emulsifier with those of a hydrocolloid. The ester is less sensitive to calcium ions than alginic acid and does not flocculate at low pH. In particular, PGA is used to thicken and stabilize acidic and Ca^{2+}-rich foods. The emulsifying effect is advantageous in producing stable foams, for example in beer (allowed limit 100 mg l^{-1}). In addition, it is approved for use in sauces for fish products (20 g kg^{-1} product) [1].

Toxicology and Regulatory Affairs

In some regions of the world, seaweed has been part of human nutrition for centuries. Alginates are neither resorbed nor metabolized in the intestinal tract. They can reduce the resorption rate of mineral cations like calcium and iron. Numerous toxicological studies have found no negative effect on human health. There is no specified ADI. Alginates are approved for use in foods in numerous countries. Specifications for alginic acid, sodium, potassium, calcium, and ammonium alginate salts and propylene glycol alginate (PGA) are listed in the USA Food Chemical Codex (FCC) and are also considered as GRAS in

accordance with US Food and Drug Regulations (CFR 21). In Europe, alginic acid, its Na, K, NH_4, and Ca salts and PGA are listed as food additives with E number 400–405 [2].

In contrast to the pure alginic acid salts, PGA has an ADI of 25 mg kg^{-1} body weight (BW) per day, because the effect of propylene glycol, formed during metabolism, on the human organism has not been fully clarified [1].

1.2.3 Carrageenan

Raw Material Origin, Manufacturing, and Quality

For centuries, red seaweeds (family Rhodophyceae) have been harvested and used in foods in the Far East and Europe. They all contain naturally occurring polysaccharides that act as structural substances that fill the voids within the cellulose structure of the plant. Beside agar and furcelleran, carrageenans are a very important group of hydrocolloids extracted from red seaweed of *Chrondrus, Gigartina,* and *Euchema* species growing close to the coasts of the North Atlantic and Pacific Ocean. Different manufacturing processes are used to make carrageenan extract and semi-refined carrageenan, also known as processed *Euchema* seaweed (PES), PNG, SRC, or ARC. The primary process difference between 'extract' and 'PES' is that the extract process solubilizes the carrageenan and removes the solids, whereas the PES process leaves the carrageenan within the seaweed cellulosic structural matrix. To manufacture refined carrageenan, the harvested seaweed is dried and washed with water to remove sand and stones. Then it is extracted with alkaline water under pressure at 100–140 °C (212–284 °F). The specific alkali, for example sodium, potassium, or calcium hydroxide, is selected depending upon the carrageenan salt to be produced. Subsequently, the raw extracts are purified by filtration, treatment with activated carbon, and centrifugation, and finally concentrated. The concentrated solutions are then precipitated with isopropyl alcohol to give a fibrous mass that is squeezed to remove the alcohol and dried. An alternative recovery process is used for κ-carrageenan whereby the solution is extruded into a concentrated solution of potassium chloride and a fibrous mass is formed. The precipitated gel mass is dewatered under pressure and may be frozen and thawed to increase dehydration before further drying and grinding. PES manufacture includes, after appropriate washing, a soaking in potassium hydroxide solution (with excess potassium cations to prevent carrageenan solubility) before chopping and bleaching to enhance the colour of the finished powder. After washing, the drying, grinding, and blending steps are the same as those for the extract carrageenan process. The microbiological requirements for PES used in foods are identical to those for carrageenan. Only requirements for the so-called alkali-modified flour (AMF) are less strict as this product is targeted for pet food and non-food applications [1,2].

The global annual production of carrageenan is about 50 000 MT, of which about 70–80% is used in the food industry.

Chemical Structure

Carrageenan is the name for a family of salts of sulfated galactans with a sulfate content of 18–40% (Table 1.3). They are all high-molecular-weight linear hydrophilic polysaccharides consisting of repeating disaccharide units of galactose and 3,6-anhydro-galactose, both sulfated and non-sulfated, joined by alternating α-(1 → 3)- and β-(1 → 4)-glycosidic links. The main carrageenan fractions are the κ-, λ-, and ι-carrageenans (kappa, lambda, and iota, respectively), which differ in number and position of sulfate ester groups and in their content of 3,6-anhydro-galactose units. In the natural state in live seaweed, unmodified κ- and ι-carrageenan contain about 30% μ- and ν-carrageenan (mu- and nu-c, respectively), which are the precursor structures in carrageenan and which are converted into κ- and ι-carrageenan by alkaline modification (reducing these precursors to less than 5%). λ-Carrageenan occurs naturally in seaweed and can be transformed into ϑ-carrageenan (theta). κ-Carrageenan consists of a chain of alternating galactose and anhydro-galactose-units where the galactose residues carry a sulfate ester group at the 4-position. Its sulfate ester content is approximately 22% and its 3,6-anhydro-galactose content is about 33%. ι-Carrageenan has an additional sulfate ester group at the 2-position on the anhydro-galactose residue and therefore has a higher sulfate ester content of 32%, along with 26% anhydro-galactose. λ-Carrageenan is an alternating chain of galactose units linked in β-(1 → 4) and α-(1 → 3) mode. The galactose at the 4-position is mainly present as 2,6-disulfate, and the galactose at the 3-position mainly occurs as 2-sulfate. It contains approximately 37% sulfate ester with little or no 2,3-anhydro-galactose. PES differs from traditional clarified carrageenan extracts in that it contains 8–15% acid insoluble matter (AIM) compared to 2% maximum for an extract. AIM makes up the structural network of plant cellulosic and proteinaceous material, maintaining its integrity during the PES process. Consequently, in applications using PES, enough energy must be applied during processing to break down the AIM structure and release the carrageenan. Hydration and solubility profiles are different for carrageenan and PES. For applications requiring clear solutions or gels, only carrageenan extract can be used. The average molecular weight of carrageenan and PES is between 200 and 800 kDa, but it can be as high as 1.5 million daltons (MDa). κ-Carrageenan is the most used of these seaweed extracts. λ-Carrageenan is the least utilized; its production is very expensive because special plants need to be selected. Most commercial products labelled 'λ-carrageenan' are blends of non-gelling unmodified κ-types and λ-types [1,2].

Solubility, Viscosity, and Gelation

The solubility of carrageenans depends on their structure, the applied temperature, and the presence of cations. All carrageenans are soluble in hot water, but – with the exception of λ-grades, only the sodium salts of κ- and ι-carrageenan are soluble in cold water. Potassium and calcium salts of κ- and ι-types are completely soluble at 50–60 °C (122–140 °F). All carrageenans are soluble in hot milk. In cold milk, only λ-carrageenan has solubility, producing a thickening effect via protein interactions, an effect that is enhanced by phosphates.

Table 1.3 Characteristics of κ-, ι-, and λ-carrageenan.

	κ-, ι-, and λ-carrageenan
E-No.	E 407
Origin	Seaweed extract
Chemical composition	• Family of salts of sulphated galactans (high sulfate content 18–40%); • D-galactose, D-(3 → 6)-anhydro-galactose, sulfate ester groups
Nutritional value (in 100 g) – metabolism	0 kJ (0 kcal); no resorption
Fibre content	100% Soluble fibre
Toxicology	Global approval as food additives; viscosity: minimum 5 mPa s as 1.5% solution at 75 °C (167 °F) (average MW of 100 kDa); Europe: ADI (75 mg kg^{-1} BW per day) and MW limit of maximum 5% below 50 kDa
Solubility at low temperature (H_2O)	κ-C: only Na^+ salts are soluble, limited swelling of K^+ and Ca^{2+} salts; ι-C: only Na^+ salts are soluble, Ca^{2+} salt gives thixotropic swollen particles; λ-C: all salts are soluble in cold water
Appearance of an aqueous solution	Clear for pure extracts, opaque-turbid for PES
Viscosity of solution in water	Medium to high (hot solutions set to gels when cooling)
Impact of heat on viscosity in water (pH 7)	All κ-, ι-, and λ-C types are completely soluble in water and milk at $T = 80$ °C (176 °F)
Viscosity development in water at pH 7 ($T = 0$–100 °C)	Complete solubility in water (or milk) at $T = 80$ °C (176 °F), viscosity is reduced by further heating (fully reversible at pH 7–9), solutions of κ- and ι-types set to gels upon cooling, gels are stable at room temperature, gels melt by heating and re-set upon cooling without loss of gel strength or texture in neutral conditions
Shear stability	Solutions are pseudoplastic (reversible shear-thinning); κ-C-gels break when sheared (irreversible); ι-C-gels break by shear, but recover and re-gel after shear stress is removed
Thickening effect	High
pH stability	Medium (pH 5.5–9)
Decomposition	κ-C + ι-C: hydrolysis by acid (accelerated by heat, low pH value, and time); however, gels are acid-stable; λ-C: hydrolysis in acidic systems
Film formation	High
Emulsion stabilization	High
Gelation	κ-C: strongest gels with K^+; ι-C: strongest gels with Ca^{2+}; λ-C: no gelation with cations (but gelling with very high salt concentrations)
Gel strength and gel stability	κ-C: firm brittle gels with strong synaeresis, not freeze–thaw stable, hysteresis 10–20 °C (18–36 °F);

Table 1.3 (*Continued*)

	κ-, ι-, and λ-carrageenan
	ι-C: soft elastic texture, no synaeresis, freeze–thaw stable; λ-C: no gels, solutions are freeze–thaw stable
Gel transparency	High
Tendency for gel synaeresis	κ-C-gels: strong synaeresis; ι-C-gels: no synaeresis
Impact of electrolytes (cations +, 2+, 3+)	κ-C: strong gelation with monovalent potassium ions; ι-C: strong gelation with divalent calcium ions; λ-C: no impact
Reaction with Ca^{2+} ions	Gelation with ι-carrageenan
Protein activity	κ-C. forms weak gels with κ-casein in milk to stabilize neutral dairy products and particles in suspensions; ι-C. and λ-C. have a strong protein interaction in acid
Crystallization control	Gels of ι-C. and solutions of λ-C. are freeze–thaw stable, gels of κ-C. exhibit synaeresis
Synergistic effects with other hydrocolloids	κ-Carrageenan forms synergistic gels (increased gel strength and elasticity, reduced synaeresis) with galactomannans (e.g. LBG) and konjac glucomannan; synergism between starch and ι-carrageenan
Other synergistic effects	Solubility in 50% sugar solutions: κ-C. is hot-soluble, ι-C. is insoluble, λ-C. is soluble; solubility in 10% salt solutions: κ-C. is insoluble, ι-C. and λ-C. are hot-soluble
Negative interactions	—
Dosage level in foods	Low to medium (typical 0.02–3%)

In principle, when a carrageenan dispersion is heated, there is no significant particle swelling or hydration until the temperature exceeds about 40–60 °C (104–142 °F). As the particles hydrate, the viscosity increases as the swollen particles offer more resistance to flow. Further heating to 75–80 °C (167–176 °F) produces a drop in viscosity. On cooling the solution shows a marked increase in viscosity followed by gelation below 40–50 °C (104–122 °F).

Carrageenan solutions are highly viscous and viscosity is reduced with increasing temperature. The viscosity drop is reversible when heat is applied in neutral systems (pH 7–9). At room temperature viscosity is stable over a wide pH range. Acid and pH values below 4.5–5.5 lead to hydrolysis of the carrageenan solutions with heat accelerating the degradation, but the gels of κ- and ι-types are acid-stable. On this account, carrageenan should be added to acidic products at the last moment or acid should be added to the food immediately before filling in order to minimize polymer breakdown.

Pure solutions show pseudoplasticity or shear-thinning when pumped or stirred.

All carrageenans hydrate at high temperatures, with κ- and ι-types in particular exhibiting a low fluid viscosity in both water and milk. On cooling to below the gel point, which is between 30 and 70 °C (86–158 °F), these κ- and ι-carrageenans set to form a range of gel textures depending on the cations and other

ingredients present. In the presence of potassium (K^+), κ-carrageenan forms firm, brittle gels that exhibit synaeresis and are not freeze–thaw stable. ι-Carrageenan gives soft, elastic syneresis-free gels with calcium (Ca^{2+}). κ-Carrageenan gels break when sheared and this effect is permanent. ι-Type gels break by shear but recover and re-gel after shear stress is removed, indicating thixotropic behaviour, but with a longer time to recover fully than, for example, xanthan gum. Both gels are stable at room temperature but can be remelted by heating to 5–30 °C (9–54 °F) above the gelling temperature. On cooling, the system will re-gel without loss of gel strength or change in texture under neutral conditions. Sugar and salt affect the solubility of carrageenans. In 50% sugar solution, κ-types are hot-soluble, ι-types are insoluble, and λ-types are soluble. In 10% salt solutions, κ-carrageenan is insoluble and ι- and λ-types are hot-soluble. Salts and sugar have a strong effect on the hydration temperature of carrageenan and on its subsequent setting and remelting temperatures. For example, 2% salt (NaCl) can increase the hydration temperature of the sodium salt of κ-carrageenan from 40 °C (104 °F) to 55 °C (131 °F) or higher in meat brines. At concentrations of 4% NaCl or above, hydration is fully prevented. The presence of high solids, in confectionary for example, effectively concentrates the carrageenan and cations on the aqueous phase so that gelation may occur at 80–85 °C (176–185 °F) or higher. To ensure full hydration and prevent lumping, carrageenan particles are premixed with sugar (5–10 times amount) or pre-dispersed in oil, sugar syrup, alcohol, or a salt solution [2].

Properties

The ability of κ- and ι-carrageenans to form gels in the presence of K^+ and Ca^{2+} ions forms the basis of many applications in food. Gelation is caused by the relatively high content of hydrophobic anhydro-galactose residues at low to medium content of sulfate ester groups. The gelation mechanism consists of two steps. Gel-I is an intermediate step including formation of zones of single helices by ionic interaction and spiral-like association of different molecules. In the final gel-II state, the single helices arrange with adjacent ones to form double or triple helical structures. Calcium ions induce divalent bridging between adjacent chains in ι-types, while potassium ions counter sulfate charges without sterically hindering close approach and double helix formation. Hydrogen bonding occurs between different helices.

κ-Carrageenan forms synergistic gels with galactomannans such as locust bean and tara gum, as well as glucomannans such as konjac flour. These gels have an increased gel strength and elasticity, while synaeresis is reduced. The optimum blend ratio is 60 : 40 to 70 : 30 of κ-carrageenan to mannan gum.

Of note is the interaction of κ-carrageenan with κ-caseins of milk at around neutral pH. This protein and milk reactivity is due to electrostatic attractive forces between the negatively charged hydrocolloid with the positively charged regions of κ-caseins. Already at very low concentrations of 0.01%, κ-carrageenan forms a weak gel of fluid character. Additionally, κ-carrageenan builds structure by interacting directly with positively charged amino acids and indirectly, via

divalent cations, with negatively charged amino acids in the proteins at the surface of the casein micelles. Very low levels (0.015–0.025%) are sufficient to prevent whey separation during processing and storage of ice cream, milk shakes, cream cheese, and dairy desserts. This 'liquid gel network' can also stabilize particles such as cocoa in chocolate milk and other suspensions at only 0.02% without increasing viscosity significantly and without phase separation or sedimentation [2].

Applications

Carrageenans are used as gelling and thickening agents for water-based jellies and for dairy products such as desserts, puddings, ice cream, mousses, whipping creams, cheese spreads, cream cheese, infant formula, and neutral milk drinks (e.g. calcium-enriched milk, nutritional beverages, chocolate milk, and milk shakes). They are applied in soups, sauces, and salad dressings, especially in transparent low-viscosity products with herbs/spices. Carrageenan is used successfully in meat products such as cooked ham where it stabilizes the injected water. The clarification of beer and fining of wine are other applications.

Toxicology and Regulatory Affairs

Carrageenan and semi-refined carrageenan (PES) have a long history of use and are permitted globally for use in food. Carrageenan is not assimilated by the human body, providing only fibre with no nutritional value.

In the European Union, carrageenans are approved as E 407 (and E 407a for PES) as food additives with unrestricted level (quantum satis). In the USA, the US Food and Drug Administration makes no distinction between carrageenan and PES and both are regulated as carrageenan.

In the past, carrageenan was rated as harmless by the independent Expert Committee of FAO/WHO and by the US FDA. But, more recently, in animals, ulceration and changes in the immune system have been observed with degraded carrageenan. When carrageenan is heated at high temperatures and at low pH, degraded carrageenan (so-called polygeenan with MW of 10–20 kDa) is produced. The longer the heating, the more the molecule length of carrageenan is reduced. Therefore, an ADI of 75 mg carrageenan per kg of body weight per day has been set. Additionally, JECFA (Joint FAO/WHO Expert Committee on Food Additives) and SCF (Scientific Committee of Food, in Europe) have limited the viscosity of a 1.5% solution to a minimum of 5 mPa s at 75 °C (167 °F), which corresponds to an average molecular weight of 100 kDa. A limit for the MW is set with a maximum of 5% below 50 kDa. Commercial carrageenan and PES normally have MW in the range 200–800 kDa. However, it is also found that the presence of associated cations prevents carrageenan hydrolysis during digestion and that normal food processes do not significantly increase the proportion of low-molecular-weight material [2].

There are claims that carrageenan hinders the absorption of minerals such as potassium and can cause allergies.

1.2.4 Pectins

Raw Material Origin, Quality, and Manufacturing

Pectin was discovered as a gelling agent in 1820. It is widely distributed in the tissue of land plants, where it acts in combination with cellulose as an intercellular matrix substance (cell walls, middle lamellae). For commercial use, pectin is primarily extracted from apple pomace (15% pectin) and citrus peel of lime, lemon, or orange, which contain about 30%. Sugar beet pulp with 20% pectin is used to a lesser extent. All raw materials are by-products from other industries of fruit juice or sugar production. Most pectin is manufactured be extraction with hot aqueous acid solution at 50–90 °C (122–194 °F) for 3–12 h at pH 1–3. Insoluble protopectin is degraded to soluble pectin by this method. The raw extract is filtrated. Potentially available starch is enzymatically degraded and thus removed. The purified extract is concentrated and drum- or spray-dried. Another option is to precipitate the pectin by alcohol. The precipitation method results in highly pure products and is preferably used today. By modifications during extraction process and controlled partial de-esterification, pectins can be produced with different degrees of esterification and polymerization. Amidated pectin is typically obtained by amidating conventional pectin with ammonia in an alcoholic suspension. More recent technology includes methyl de-esterification with biocatalysts.

The annual production of more than 45 000 MT is mainly for food use [1,2].

Chemical Structure

The substance class of pectins occurs in various structures (Table 1.4). Plant species, environmental conditions, and plant maturity have an impact. Common to all pectins is linear polysaccharides whose main component is the α-D-galacturonic acid (pK_a 3.5) as a monomer. According to a European directive, commercial pectin is classified as a substance that contains at least 65% galacturonic acid. Pectin is a polyuronide consisting of a linear backbone of α-(1 → 4)-linked galacturonic acid units. The carboxy groups (COOH) are partially esterified with methanol (to give the $-COOCH_3$ group). The secondary hydroxyl groups may be partially esterified with acetate depending on the origin of the pectin. Covalently bound side chains of neutral sugars (xylose, β-(1 → 4)-D-galactans, α-(1 → 5)-L-arabenes) may be included in the macromolecule. Rhamnose units, linked with galacturonic acid units at the 1- and 2-positions, are integrated into the backbone. The basically quite stretched pectin molecule thereby has a kink.

When extracting pectin for commercial use, most of the neutral sugar side chains are removed. Thus, commercial pectin is often referred to as the homogalacturonic backbone. By weight, typically more than 70% of these pectins is galacturonic acid, and, depending on pectin quality and origin, up to 75% of the galacturonan groups are methyl esterified. According to the

Table 1.4 Characteristics of pectins.

	Pectins
E-No.	E 440
Origin	Fruit extract
Chemical composition	• Linear polyuronide, partially esterified with methanol and acetate; • backbone of galacturonic acid
Nutritional value (in 100 g) – metabolism	0 kJ (0 kcal); no resorption
Fibre content	100% soluble fibre
Toxicology	No health concerns, ADI value 'not specified'; considered as natural component of foods
Solubility at low temperature (H_2O)	HMP: cold water soluble; LMP: only soluble as Na or K salt
Appearance of an aqueous solution	Opaque, yellowish
Viscosity of solution in water	Depends on concentration (low at 0.5%, high at 3–4%)
Impact of heat on viscosity in water (pH 7)	Irreversible reduction of viscosity and gelation power due to molecular degradation
Viscosity development in water at pH 7 ($T = 0$–$100\,°C$)	• Ca^{2+}-free: high-viscosity solution; • gel formation in presence of calcium
Shear stability	High, but reversible shear-thinning
Thickening effect	Low – thickening only after gelation
pH stability	Low (HMP: 2.5–4.5, LMP: 2.5–5.5)
Decomposition	• Acid or alkali (only stable at pH 3.5–5); • high temperatures; • many enzymes
Film formation	High
Emulsion stabilization	High for pectins with high acetyl content
Gelation	HMP: with sugar + H^+ LMP (amidated or non-amidated): with Ca^{2+} ions
Gel strength and gel stability	HMP: – no gelation at pH > 3.5; firm thermo-irreversible gels at pH < 3.5 LMP: • non-amidated: spreadable, thermoreversible; • Amidated: semi-firm to spreadable, reversible
Gel transparency	High
Tendency for gel synaeresis	Low
Impact of electrolytes (cations +, 2+, 3+)	+ Metal ions (2+/3+): precipitation or gelation
Reaction with Ca^{2+} ions	HMP: no reaction; LMP: gel formation
Protein activity	High for HMP (solubilizing effect around IEP + heat protection effect at acidic pH)
Crystallization control	Freeze–thaw stable gels are possible
Synergistic effects with other hydrocolloids	Alginate forms strong thermoreversible gels with HM pectin (pH < 4) at low solid levels and with LM pectin at pH < 2.8
Other synergistic effects	Crosslinking of pectin molecules with positively charged molecules (chitosan, poly-L-lysine)
Negative interactions	Precipitation with gelatine and CMC (only HMP)
Dosage level in foods	Medium (0.5–5%)

number of carboxyl groups being esterified with methanol, the class of pectins is divided into:

- high-esterified pectins (HM pectin) with a methoxyl content >7% and degree of esterification >50% (typically 55–75%);
- low-esterified pectins (LM pectins) with a methoxyl content <7% and degree of esterification <50% (typically 20–45%).

Additionally, amidated LM pectin can be prepared by treating pectin with ammonia during processing to convert some of the C6 methyl ester groups into amide groups. Values for amidated LM pectin are 30% degree of methyl esterification and 20% degree of amidation. Another way of differentiating pectins is by the degree of acetylation.

The molecular weight of commercial products is between 30 and 300 kDa [1,2].

Solubility, Viscosity, and Gelation

In general, pectin is soluble in water or forms a colloidal solution. It is insoluble in alcohol and most organic solvents. Powdered pectin tends to form lumps when added directly to water. As concentrated pectin exhibits non-Newtonian behaviour and the viscosity decreases with increasing rates of shear, a high-speed mixer is useful. By applying high shear forces, solutions of up to 10% can be prepared; without such forces it is difficult to obtain smooth pectin solutions above 3%, owing to the high viscosity impeding dispersion. Preparation of dry blends with sugar (ratio of sugar to pectin = 5 : 1) or prewetting in liquids in which pectin is insoluble are alternative hydration methods. Pectins form both soluble and insoluble salts. Sodium pectinates are more soluble than pectic acids, which, in turn, are more soluble than calcium pectinates. LM pectins have a lower solubility – they are only soluble as sodium or potassium salt. Sodium, potassium, and other monovalent ions are bound electrostatically to the pectin backbone, whereas divalent cations are involved in gelation of pectin, visualized as the so-called egg-box model. As a general rule, high levels of soluble solids and salts decrease pectin solubility. The addition of sequestering agents such as pyro- or ortho-phosphates improves the hydration of pectin under such adverse conditions. Pectin creates viscous solutions. The viscosity depends on concentration and increases greatly above the concentration at which the molecules entangle. A weak solution (<0.5%) exhibits almost Newtonian behaviour, whereas concentrated solutions are shear-thinning. The viscosity also depends on pectin type, solvent, pH value, temperature, and presence of salts. Polyvalent ions like calcium generally increase viscosity because of crosslinking of the polymer chains.

Pectin has optimal stability at pH 3.5–4.0, the natural pH of fruit preserves, and slowly degrades outside this range. In neutral and alkaline conditions, the homogalacturonic backbone depolymerizes by β-elimination, a process in which the backbone glycosidic bonds at the C4 position of methylated galacturonic acid units are cleaved. As a consequence, HM pectin is more vulnerable to β-elimination than LM grades. At elevated temperature, depolymerization at the

pectin backbone starts at pH 5, although pectin is more robust at room temperature. In acidic conditions (pH <3), methyl ester and acetyl groups are cleaved and the neutral sugars are hydrolysed even at low temperatures. At elevated temperatures, the degradation reactions accelerate. Evidently, high pH values and high temperatures are unfavourable parameters for pectin stability [2].

Properties

Pectin is a weak acid with polyelectrolyte behaviour. At neutral pH, pectin is negatively charged and occurs as polyanion. Because of the negative charge of pectins, they react with positively charged polymers, including proteins. This feature is utilized in acidified milk drinks.

The most important property of pectin is its ability to gel. To induce gelation, high-esterified pectins require low water activity due to high sugar levels (55–85% soluble solids) and an acidic pH of 2.5–3.8. Gelation results from diminished electrostatic repulsion and is caused by hydrogen bonding between non-dissociated carboxyl groups and secondary alcohol groups together with hydrophobic interactions between methyl ester groups. The degree of methyl esterification is fundamental for gelling HM pectin. Increased esterification degrees and low pH enhance the ability to gel. For this reason further groupings have been established. The sub-groups include ultra-rapid set, rapid set, medium rapid set, slow set, and extra-slow set pectin with the degree of methyl esterification ranging from 74% to 77% for ultra-rapid set types to 58–60% for extra slow set pectins. For a given pH, setting time increases and setting temperature decreases with decreasing degree of methyl esterification. Gels of HM pectin are formed at 25–90 °C (77–194 °F) and are thermo-irreversible. Gels are of a firm texture at pH below 3.5. Above pH 3.5, no is gel formed, but viscosity is provided.

Low-esterified pectins gel over a broader pH range of 2.5–6 and at lower concentrations of sugar (5–65%) but require the presence of cations, which in terms of food is generally calcium. Magnesium ions do not initiate gelation. Since the calcium reacts with de-esterified galacturonic acid units, a low degree of methyl esterification enhances the ability to gel and the more calcium sensitive the pectin becomes. Low pH favours gelation of LM pectin, but gelling is possible up to pH 6. Gels of non-amidated LM pectin are formed at a soluble solids range of 25–55% and 40–100 °C (104–212 °F). These gels are, depending on the calcium level in the system, thermoreversible. The gels are soft and spreadable above pH 3.5. Firmness increases when pH is lowered (<3.5).

Amidated LM pectin gels at lower pectin concentration and lower soluble solids content (5–65%). Gelation requires less calcium than for non-amidated LM pectin. Amidated products are less sensitive to high calcium levels (no precipitation). Gels are formed at 30–70 °C (86–158 °F) and are always thermoreversible. Gels above pH 3.5 are spreadable and similar to gelled non-amidated LM pectin. Below pH 3.5, gels are semi-firm and similar to HM pectin but more rubbery.

Pectic acid has a degree of esterification below 5% and gels like LM pectin. It precipitates at high pH values and high levels of polyvalent cations as salts (pectates).

The presence of acetyl groups may prevent pectin gelling, but makes pectin a useful emulsifier. The acetyl groups enhance the hydrophobic nature of the molecule and provide a surface-active character. Thus, pectin is able to act as interfacial agent in the stabilization of oil–water or air–water systems.

Generally, pectin does not show any synergy with other hydrocolloids, but its gel strength might be influenced by addition of other substances. It is worth mentioning that HM pectin forms strong thermoreversible gels with high-polyguluronic acid alginate at low solid levels and pH <4. LM pectin gels with these alginates at pH <2.8. More interactions can be found between pectin and positively charged molecules such as chitosan and poly-L-lysine, which are able to crosslink pectin molecules. Such interactions may find use in films [2].

Applications

Pectin is used as gelling, thickening, and stabilizing agent in foods and, to a lesser extent, in pharmaceuticals. Basically it controls moisture content and helps to create the desired texture. HM pectin gives structure, bite, and bake-stability to acidic jams, jellies, and confectionary with high sugar content. It is used as non-gelling stabilizer in acidified dairy or soya drinks and in fruit beverages. In bread and frozen dough, HM pectin improves volume, retains moisture, softness, and freeze–thaw stability.

LM pectin thickens fruit-based ripples and toppings with pumpable consistency. Other applications are fruit preparations for yogurt and cold-setting milk desserts. In low-fat products, LM pectin acts as fat substitute in sauces, dressing, ice cream, processed meat and cheese products, and spreads. Amidated LM pectin types find use as gelling and foaming agents in non-fruit confectionary (marshmallows, toffee, and peppermint). Amidated pectin gels are more robust than gels of non-amidated pectin types. Furthermore, pectin may be used to purify and concentrate protein solutions by exploiting the electrostatic repulsion effect at pH values above the isoelectric point [2].

Commercial products often contain sugar to adjust gel strength and buffering salts to adjust setting time.

Toxicology and Regulatory Affairs

Pectin is a soluble dietary fibre and a natural part of the human diet, but does not contribute significantly to nutrition. The daily intake of pectin from fruits and vegetables can be estimated to be around 5 g assuming a consumption of approximately 500 g fruits and vegetables per day. In human digestion, pectin binds to cholesterol in the gastrointestinal tract, slows glucose absorption by trapping carbohydrates and thus attenuates blood glucose response. Consumption of pectin has been shown to reduce blood cholesterol levels. The mechanism appears to be an increase of viscosity in the intestinal tract, leading to a reduced absorption of cholesterol from bile or food. In the large intestine and colon, microorganisms degrade pectin and liberate short-chain fatty acids that have a positive influence on health (prebiotic effect). Improved mineral absorption, reduction of gastric emptying time, and anti-diarrhoea effects are additional favourable physiological effects reported.

Pectin is regarded as a safe food additive and has been given an acceptable daily intake (ADI) of 'not specified' by the committees of FAO/WHO and European Union. Furthermore, the US FDA accords pectin 'generally recognized as safe' (GRAS) status. Notably, the Codex Alimentarius and US specifications include both amidated and non-amidated pectins in one class. EU legislation distinguishes between non-amidated and amidated pectins. Nevertheless, both types are labelled as E 440 and permitted uses are identical, except for organic foods, where only non-amidated pectin is permitted [2].

1.2.5 Native and Modified Starches

Raw Material Origin and Manufacturing

Starch is widely used in plants as a reserve carbohydrate in various organs. The starch granules formed in the amyloplasts of plants consist of concentric or eccentric layers of different density and have different sizes (2–150 μm), size distributions, and shape. The quantitatively most important raw materials are corn, waxy maize, potato, cassava, wheat, rice, waxy rice, and tapioca. In addition, starches are extracted from peas, lentils, sweet potatoes, sago palms, lotus roots, mung beans, water chestnuts, sorghum, arrowroot, kouzu, taro, and edible canna.

The manufacture of a starch depends on the location of the reserve material in the specific plant. In some cases, for example potato, the starch granules occur free in the cells, so that their isolation is a relatively simple process. The plant material is crushed, the starch is slurried with water, separated from the suspension (starch milk), and dried.

In other cases, for example cereals and corn, the starch is stored in the endosperm incorporated into a protein matrix and, thus, extraction is more difficult.

Maize, for example, is soaked for about 48 h in warm water (50 °C (122 °F)). To break up the protein matrix, the soaking water contains SO_2 (about 0.2%). This speeds up the process and increases the starch yield. Subsequently, the corn kernels are crushed and the germs that are rich in fat are separated by flotation. Gluten (protein) and starch are separated in hydrocyclones due to their density difference. The starch is washed and dried.

Modified starch is the most used food hydrocolloid, with a volume of more than 1.5 million tons. The global volume of native and modified starches is estimated to be about 80 million tons (78% corn, 11% tapioca, 7% wheat, and 4% potato).

Chemical Structure of Native Starches

Starches are long-chain polymers of α-D-glucopyranose units with the general molecular formula $(C_6H_{10}O_5)_n$ (Table 1.5). Starch is a mixture of two glucans – amylose and amylopectin – the content of which depends on the plant source. While the average amylose content is 20–30%, there are so-called amylo-varieties with 50–80% amylose. Normal starches contain 70–80% amylopectin, but the so-called waxy varieties have 99% (only 1% amylose) due to breeding measures. Amylose can be extracted from starch by, for example, crystallization

Table 1.5 Characteristics of native and modified starches.

	Native starches	Modified starches
E-No.	—	E 1400 Following
Origin	Seed extracts (germs, roots)	
Chemical composition	α-D-Glucose	
Nutritional value (in 100 g) – metabolism	1507 kJ (360 kcal); fast resorption	1750 kJ (418 kcal); fast resorption
Fibre content	1% (~86% glucose)	0% (~100% glucose)
Toxicology	No health concerns; no ADI specified; GMO – freedom of raw material is an issue	
Solubility at low temperature (H_2O)	Cook-up starches are insoluble; development of cold-water soluble instant starches	
Appearance of an aqueous solution	Turbid suspension that sediments at room temperature, slurry needs cooking to dissolve	
Viscosity of solution in water	Low at room temperature (only pre-gelatinized native and modified starches are cold water soluble)	
Impact of heat on viscosity in water (pH 7)	Swelling + gelling (at $T > 60$ °C (140 °F)); formation of heat-stable gels	
Viscosity development in water at pH 7 ($T = 0$–100 °C)	Swelling + gelling (at $T > 60$ °C (140 °F)); formation of heat-stable gels	
Shear stability	Low after gelation, irreversible viscosity loss	Shear-stable starches are available
Thickening effect	High	
pH stability	Low after gelation	
Decomposition	• Cooking in acidic or alkaline systems ($6 > pH > 8$); • oxidation by free radicals; • high shear forces; • enzymes	
Film formation	High	
Emulsion stabilization	No – only by thickening	Emulsifying starches are available
Gelation	Upon heating	
Gel strength and gel stability	High gel strength + high stability during cooking, baking, cooling	
Gel transparency	Low	
Tendency for gel synaeresis	High	Medium
Impact of electrolytes (cations +, 2+, 3+)	Low	
Reaction with Ca^{2+} ions	No	
Protein activity	Low/no	
Crystallization control	No – syneresis	Medium
Synergistic effects with other hydrocolloids	With gelatine: improved gelation, with guar: viscosity increase, with MC: reduced boiling, improved freeze–thaw-stability	
Other synergistic effects	Sugar increases the temperature of gelation	
Negative interactions	Formation of acrylamide: heating (>120 °C (248 °F)) in presence of the amino acid asparagine (promoted by fructose and glucose)	
Dosage level in foods	High (typical 1–5%)	

from a starch dispersion, usually in the presence of salts ($MgSO_4$) or polar organic compounds (butanol or low molecular weight fatty acids), which form complexes with amylose and can be fractionated precipitated. About 70% of the mass of a starch grain is considered to be amorphous (disordered regions) and 30% to be crystalline (high degree of orientation). Amylose is water soluble and made of helical, but unbranched chains of 1000–10 000 glucose residues with $\alpha(1 \rightarrow 4)$ linkage. The molecular size depends on the source of raw material. The length is about 0.5 µm, the molecular weight about 0.15–1.5 million daltons (MDa). The water-insoluble amylopectin consists of branched chains of glucose residues in $(1 \rightarrow 4)$- and $(1 \rightarrow 6)$-α-glycosidic bonds. On average, there is a branch point every 15–30 glucose residues. A phosphate residue occurs on about every 400th glucose residue. The structure is supposed to be a double helical with a parallel arrangement (globules about 0.05 µm in diameter). The crystallinity of starch is caused mainly by amylopectin. The molecular weight is very high and in the range 10–700 MDa.

Native corn starch has 25–28% amylose with a DP (degree of polymerization) of 2000 and 72–75% amylopectin with a DP of 2 million. Native tapioca starch consists of 17% amylose (DP of 5000) and 83% amylopectin (DP 3 million) [2].

Modification

The properties of native starch and various starch fractions (amylose, amylopectin) can be improved by physical or chemical modifications and adjusted to defined uses. Some modifications include several conversion processes (e.g. acetylated oxidized starch). A modification can be made on the native starch granule or after gelatinization. For starches, the functional properties change already when only a few new groups are incorporated into the molecule. The aim of modification is an increased tolerance and stability of the starch against the effects of temperature (heat/cold), shear forces, and changes in pH (acid addition). For regulatory reasons, the declaration is significantly different between chemically and physically modified products. Physically modified starches are handled like native starches because they are 'only' treated with physical methods (heat, pressure, water). Instant or pregelatinized native starches are an example. In the chemical modification of cook-up and instant starches, there is a distinction between 'stabilization' and 'crosslinking'. Stabilization aims to improve the storage stability. The shelf life is extended by introduction of foreign groups such as acetyl, phosphate, or hydroxypropyl with placeholder function. Products exhibit a delayed retrogradation, increased freeze–thaw stability, and enhanced mouthfeel. Examples are starch acetates and hydroxypropylated starches. The crosslinking process with adipates and phosphates increases the process tolerance. The stability to heat, shear forces, and acids is significantly improved. Crosslinked starches are characterized by a short texture. The denser the network, the more process-tolerant the resulting starch will be and the more difficult it will be to gel this specific starch. Stabilization and crosslinking can be combined to produce highly storage- and process-stable starch products (e.g. acetylated distarch adipate and hydroxypropylated distarch phosphate).

Starch-Based Products

There are several starch derivatives available. The most important are explained below.

By acidic hydrolysis of starches, dextrins and maltodextrins are produced that are used as adhesives and fat substitutes.

Starches are partially damaged by mechanical forces and pressure, for example by an extrusion process, used to improve cold dispersibility and ease of handling in bakery applications.

Thin-cooking starches result after partial hydrolysis with acid and are applied in protective films.

Starch ethers like hydroxyethyl or hydroxypropyl derivatives are formed by treatment of 30–40% starch suspensions with ethylene or propylene oxide in a strongly alkaline system (pH 11–13) with alkali metal hydroxides. The substitution varies between 0.1 and 1 mol of alkyl groups per mole of glucose. By introduction of hydroxyalkyl groups, often in combination with light crosslinking, the swelling capacity, solubility, and freeze–thaw stability are significantly improved, while the gelatinization temperature is reduced. Frozen foods and heat-sterilized canned foods are preferred applications. By reaction of starch with monochloroacetic acid in an alkaline medium, carboxymethyl starches are manufactured that are very soluble in cold water or ethanol and form gels.

Starch monophosphates are produced by dry-heating of starch with alkali orthophosphates or alkali tripolyphosphates to 120–175 °C (248–347 °F). Esters of starch are prepared by reaction with organic acids (e.g. acetic acid, higher fatty acids, (C_6–C_{26}), succinic acid, adipic acid, and citric acid), suitable activated derivatives of the acids (such as vinyl acetate), or by heating starch with the acids or their salts. The thickening ability of the esters is better than that of native starch. They have high freeze–thaw stability. Starch esters are applied for thickening and stabilization of baked goods, dried soups and sauces, desserts, preserves, margarine, and canned food. They form protective coatings on dried fruits and can encapsulate flavours.

Crosslinked starch results from the reaction of starch with bifunctional or polyfunctional reagents. Suitable substances are special phosphates or mixed anhydrides of acetic acid and dicarboxylic acids like adipic acid. Depending on the degree of crosslinking, the gelatinization temperature is increased, while the swelling capability is reduced. The stability to shear forces and extremes of pH is improved. Crosslinked starches are used in applications that require large process stability.

Oxidized starch is produced by reaction of starch with an alkaline hypochlorite solution at temperatures below the gelation point. Hydrolysis and oxidation lead to products having carboxyl groups (on average 1 to 25–50 glucose residues). In contrast to a thin-boiling product, an oxidized starch exhibits neither retrogradation nor gel formation. It is used as a low-viscosity filling material in salad dressings and mayonnaise.

Emulsifying starches or OSA (= starch sodium octenyl succinate) starches result from reaction of starch with sodium octenylsuccinate. They are readily soluble in cold liquids and can stabilize multiphase mixtures such emulsions and foams.

Cyclodextrins (CDs) are a class of compounds belonging to the cyclic oligosaccharides. They are degradation products of starch in the shape of a ring and consist of α-(1 → 4)-glycosidically linked glucose molecules (6–8 monomers). β-Cyclodextrins with seven rings are used most often. The hydrophilic groups are directed to the outside, the hydrophobic groups to the inside. The result is a toroidal structure with a central cavity. Active ingredients can be microencapsulated by inclusion and be protected or 'neutralized' when having an unpleasant smell or taste.

Solubility, Viscosity, and Gelation

Native untreated starch, so-called cooking starch, is insoluble in cold water and will only form opaque suspensions with a strong tendency to sediment. When this suspension is heated, it passes through the gelling point of the starch, which is the temperature at which it starts to swell. As the starch granules swell they absorb water until they reach their maximum size. At this point the maximum thickening viscosity is achieved. As heating continues, the starch granules cannot swell any further and so they start to break down. If this process is continued long enough all the granules break down and the amylose and amylopectin polymers are released into the solution. When this solution cools, it tends to set to give a gel-like structure [2].

Only when boiling in water does starch forms colloidal solutions, which form a gel during cooling. This process is called gelatinization. By pre-gelatinization and subsequent drying (on drums or spraying), so-called instant starches are produced that swell and hydrate even at cold temperatures.

Starches form high-viscosity solutions.

Properties

Upon heating, starches can physically bind many times their own weight of water, as they swell and gelatinize. When the aqueous suspensions are heated, the starch swells at 47–57 °C (116–134 °F), the layers burst, and at 55–87 °C (131–188 °F) a starch paste is produced. Potato starch gelatinizes at 62.5 °C (144.5 °F), wheat starch at 67.5 °C (153.5 °F). Depending on the type of starch, the pastes may have various consistencies and thickening effects. The starch gels are stable at room temperature; however, they tend to separate water (synaeresis) during cold storage and freezing. The course of gelatinization depends on three factors – botanical origin of the starch, temperature, and water content of the suspension. Dried starch (1–3% water) can be heated to 180 °C (356 °F) without major changes occurring. Starch containing about 60% water is already completely gelatinized at 70 °C (158 °F).

Starch and starch-rich products exhibit retrogradation, which refers to the recovery of previously gelatinized starch. This re-crystallization is mainly caused

by the amylose of the starch because, in contrast to amylopectin, it is not composed of a three-dimensional network of glucose and therefore the water is not bound so strongly. Amylopectin, however, forms stable gels with no tendency to retrogradation. Retrogradation is the primary reason for the staling of bread and pastries. In the flour, the starch present partially releases the physically bound liquid and transitions into the crystalline state. The consistency becomes dry and rubbery. Retrogradation of the starch is strongly favoured by cool temperatures. Between −8 and +8 °C (17–46 °F) the ageing is reinforced by a factor of three. The recrystallization can be reduced by addition of fats, emulsifiers, and thickening agents, such as guar gum, CMC (carboxymethylcellulose), HPMC, or xanthan gum.

Starch (native and modified) is detected by iodine with the iodine–starch-reaction. In the presence of starch, an inclusion compound of iodine–starch is formed that is visible due to a dark blue or blue–violet to black colour.

Applications

Traditionally, starches are used as thickening and gelling agents in all kinds of foods.

They control the rheology in soups and sauces, spreads, dressings, and condiments. Starches give texture and body to dairy products like yogurt and pudding. They improve the stability of fillings and dough for bakery products. In confectionary, starches contribute to a jelly consistency in moulded products and can replace gelatine, and in chewy confections they give the appropriate gel texture and stretch. Emulsifying starches are used in flavour-oil-emulsions for application in beverages.

Toxicology and Regulatory Affairs

In the human body, the ingested starch is first degraded to glucose. Starch digestion starts already in the mouth by enzymes (α- and β-amylases). Glucose that is not transferred into energy is used in the liver to compose glycogen ('animal starch') and be stored as reserve substance. Starch delivers bout 3.6–4.2 kcal g^{-1} of energy. So-called resistant starches are available that are digested much more slowly and only partially, making less energy contribution.

Native and modified starches have wide approval from the US FDA and European Union (EU). Most producers offer different product programs for Europe and USA because local legislation may be different.

According to European food law, several starches are not permitted in the EU. In general, modified starches are considered as food additives to be used for technological purposes in unrestricted dosage ('quantum satis').

According to current knowledge, the possibly carcinogenic acrylamide is formed by overheating of starches – especially during baking, frying, roasting, and grilling – in the presence of the amino acid asparagine. Acrylamide formation is promoted by sugars such as fructose and glucose. In the manufacture of French fries it can be formed due to high temperatures. Particularly high levels of acrylamide occur when potato- and cereal-containing foods are heated dry

above 180 °C (356 °F). Although acrylamide formation starts already at 120 °C (248 °F), it rapidly increases at 170–180 °C (338–356 °F).

1.2.6 Furcellaran

Raw Material Origin, Harvesting, and Manufacturing

Furcellaran is produced from the red algae *Furcellaria fastigiata*, where it is the structural substance. The seaweed grows close the coasts of Denmark and Canada. Production started in 1943, when Europe was cut off from seaweed supply in World War II. The biggest volume is manufactured in Denmark (approx. 1000–1500 MT). The seaweed is harvested, washed, and treated with alkali to remove proteins and colouring substances. The furcelleran is extracted with hot water under pressure. The raw extract is purified by centrifugation or filtration. The extract is concentrated under vacuum. Then furcelleran is precipitated in the form of gelatinous threads by injection of the concentrated extract into a cold potassium chloride solution (1–1.5% KCl). The precipitated threads are further concentrated by freezing, pressing, or centrifuging and are finally dried. The resulting commercial product is a potassium salt that contains 8–15% free KCl. It is a colourless to yellowish, practically odourless powder with a slightly salty taste.

Chemical Structure

Furcellaran consists of D-galactose (45–54%), 3,6-anhydro-D-galactose (30–35%), and sulfates of both monosaccharides (15–20%). All commercially available products are potassium salts of furcellaran. In composition and structure, it is very similar to κ-carrageenan; therefore, it is included in the group of carrageenans. The essential difference is that κ-carrageenan has one sulfate ester residue on two sugar residues while furcellaran has one sulfate residue on three to four sugar residues. This means furcellaran has a lower content of sulfate ester groups than κ-carrageenan. The galactose- and anhydro-galactose-units of furcellaran are alternately linked by $\beta(1 \rightarrow 4)$- and α-$(1 \rightarrow 3)$-bonds as in κ-carrageenan. The polysaccharide chain can be branched. The average molecular weight is 20–80 kDa.

Solubility and Viscosity

Furcellaran can be dispersed in water to a homogeneous suspension. Full hydration requires heating to 75–80 °C (167–176 °F). During cooling, a gel is formed. Neutral solutions (pH about 7) can be sterilized without loss of viscosity. During heating in acidic systems of pH <5, the viscosity is irreversibly reduced by hydrolysis and the capability for gel formation is lost. Monovalent ions such as K^+, NH_4^+, Rb^+, and Cs^+ cause a strong increase of gel strength; Ca^+ has a lower effect. There is no gelation with Na^+. The addition of sugar has a positive influence on the gel strength.

Properties and Applications

The properties of furcellaran are very similar to those of κ-carrageenan. It is supposed to have a cleaner taste in puddings, jellies, and chocolate milk than carrageenan [1].

Furcellaran forms very good gels with milk and is added to neutral dairy desserts and beverages such as pudding and cocoa drinks. It is also very suitable for cake icings, fruit preparations, jams, and marmalades because the gel is quickly formed in the presence of sugar and is highly stabile in acidic systems. In jams, furcellaran has an advantage over pectin due to being able to form stable gels at sugar concentrations below 50–60%. The amount of polysaccharide in gels is low, 0.2–0.5%, depending on sugar content and desired gel strength. To prevent hydrolysis during heating in low pH systems, furcellaran is added as aqueous solution (2–5%) as final step to the hot and ready cooked fruit–sugar mixture.

Other application areas are reformed meat products and fillings for meat products. It is also used for protein separation during the final filtration of beer.

Regulatory Affairs

Furcellaran is misleadingly called 'Danish agar'. In Europe, it is classified as carrageenan with E 407. There is no defined ADI.

1.2.7
Larch Gum

Raw Material and Manufacturing

Larch gum is a component of the heartwood of all kinds of larches (*Larix* species). Larches contain 5–35% (on a dry matter basis) of a water-soluble arabinogalactan, a polysaccharide consisting of galactose and arabinose. The substance is manufactured by crushing the wood and countercurrent extraction with water or diluted acids. Accompanying substances such as phenols, terpenes, and ferrum are removed by treatment of the hot gum solution with active magnesium oxide. The purification can also be done by treatment of the solution with activated carbon, ion exchangers, electrodialysis, or repeated re-precipitation with ethanol. The highly purified extract is dried on drums. The resulting white to light-brown powder is tasteless and odourless [1].

Chemical Composition

Purified larch gum is a mixture of neutral polysaccharides of different molecular size. The ratio of the building blocks galactose and arabinose varies greatly – depending on type and age of the tree, the location within the tree, and the general ratio of high- and low-molecular-weight components. The ratio of galactose to arabinose is between 4 : 1 and 23 : 1. The macromolecule consists of a main chain of β-(1 → 3) linked galactose units that has side chains in α-(1 → 6) and β-(1 → 4) linkage of galactoses, arabinoses, and mixtures of both monosaccharides.

The degree of branching is high. The molecular weight is 50–70 kDa on average. The molecule is more or less spherical [1].

Solubility and Viscosity

Larch gum is easily and completely soluble in cold and in hot water. Up to 60% of the gum can be dissolved at room temperature. It exceeds the solubility of gum acacia. Even the addition of alcohol, as much as 70%, does not precipitate the polysaccharide from aqueous solution if the alcohol is added slowly under stirring.

The viscosity of highly concentrated larch gum solutions is relatively low. The viscosity of a 10% solution at 20 °C (68 °F) is below 2 mPa s. The viscosity of a 30% solution at pH 4 is 7.8 mPa s and changes only slightly to 8.1 mPa s on increasing the pH to 11. A 40% gum solution has a viscosity of 24 mPa s. The thickening effect is stable over a wide pH range (1.5–10.5) and is not sensitive to addition of electrolytes. Newtonian flow behaviour is observed at concentrations as high as 50%. At concentration above 60%, the liquid solution turns into a thick paste. These rheological properties are caused by the highly branched molecular structure and the relatively low molecular weight. Viscosities of larch gum solutions decrease with increasing temperature, but return to their original values after cooling. There is no depolymerization or irreversible breakdown of ordered structure at elevated temperature [3].

Properties and Application

Larch gum is surface active. The decrease in surface tension produced by the gum is greatest at low pH, and the addition of electrolytes enhances surface activity, with monovalent cations being more effective than divalent ones [3].

Larch arabinogalactan is a potential substitute for gum Arabic; since it is readily dispersible in water it gives low-viscosity solutions at high concentrations and has the same emulsifying properties. Options are dietetic low-sugar products because larch gum solutions show the same physical properties as sugar solutions – except for the sweetening effect and the energy content. Further applications are emulsions of flavour oils and carrier substance for highly-effective additives such as sweeteners.

For pharmaceutical applications, larch arabinogalactan has been discussed and examined as a novel immune modulator for reducing intestinal problems, improving immune defence against colds, and effectiveness in cancer tumour therapy.

1.3
Seed Flours

1.3.1
Guar Gum

Raw Material Origin, Harvesting, and Quality

Non-ionic galactomannans act as reserve carbohydrates and are found as storage polysaccharides in the cell walls of various seeds. Guar gum is one example for

this type of seed gum. It is manufactured from the endosperm of the seeds of the guar plant (*Cyamopsis tetragonolobus*, family of Leguminosae), or cluster bean. The plant is a drought-resistant annual legume that has been cultivated in India for centuries; 80% of the globally produced guar is from India. Guar pods are 3–12 cm long and contain 5–12 seeds. Depending on weather conditions, the annual guar crop fluctuates, but in average 500 000 MT of guar seeds are available. Approximately 55 000 MT per year is used as food-grade guar gum [2].

The endosperm (32–36%) is separated from the other components of the seed (20–22% hull, 43–47% germ) by milling procedures [1].

Guar gum is a yellow to light grey powder with a slight smell and taste of beans. Its solutions are opaque to turbid.

Chemical Structure

Guar gum contains 15% water (max.), % protein (max.), 7% acid insoluble residue (fibre) (max.), less than 1.5% ash, and a minimum of 75% polysaccharides (galactomannans). Guar gum is a neutral polysaccharides consisting of D-mannose and D-galactose in a molecular ratio of 1.6 : 1 (Table 1.6). The molecule consists of a linear backbone of β-(1 → 4)-linked mannose units. Single terminal D-galactose units are linked to the main backbone by α-(1 → 6)-glycosidic bonds to the 4,6-mannose units. Statistically, nearly every second mannose unit is linked to a galactose unit. Enzymatic hydrolysis, though, has shown that the galactose residues are distributed irregularly within the mannose chain. There are zones without branches and zones where every mannose building block carries a galactose residue (mostly double or triple arrangements). The average molecular weight is about 220 kDa [1,2].

Solubility, Viscosity, and Properties

Owing to its high degree of branching, guar gum has good solubility in cold water. There are high-viscosity solutions at low concentrations, which exhibit pseudoplasticity above 0.5%. Water retention capability is high. Solutions of guar gum are freeze–thaw stable. Monovalent cations have no effect, while an addition of di- or trivalent cations leads to a viscosity increase and polyols reduce viscosity. Viscosity is irreversibly reduced when guar is heated at neutral pH to above 90 °C (194 °F) or under moderate heat in acidic systems at a pH below 3.5, because the galactomannan molecule is decomposed. Cold viscosity is stable from pH 2 to 10. Borate ions cause gelation of guar gum solutions. Addition of guar gum to starch, xanthan, or CMC has a synergistic effect on viscosity of the blend. Addition of guar gum to gelling polysaccharides such as agar increases the strength and elasticity of the gels [1].

Functions and Applications

Guar gum is used as binder and thickener in ice cream, dairy desserts, soups, sauces, meat, and bakery products. There it controls texture, influences crystallization, and prevents synaeresis and phase separation. In baked goods, it prolongs shelf life and retards starch retrogradation. It is used as a processing aid in canned foods. In healthy and dietary products, guar contributes to calorie

Table 1.6 Characteristics of guar gum.

	Guar gum
E-No.	E 412
Origin	Extract of endosperm of seed (Leguminosae)
Chemical composition	• Medium-galactose galactomannan; • mannose + Galactose (ratio M : G = 1.6 : 1)
Nutritional value (in 100 g) – Metabolism	292 kJ (70 kcal); slow resorption
Fibre content	Approx. 80% (contains 10% protein)
Toxicology	No health concerns, no ADI value defined; considered as food in Asia, not as additive
Solubility at low temperature (H_2O)	Highly soluble
Appearance of an aqueous solution	Opaque, grey, cloudy
Viscosity of solution in water	High in cold water, lower in hot water
Impact of heat on viscosity in water (pH 7)	Viscosity decrease
Viscosity development in water at pH 7 (T = 0–100 °C)	Irreversible viscosity loss at T > 90 °C (194 °F)
Shear stability	Pseudoplastic > 0.5% concentration, shear thinning
Thickening effect	High
pH stability	High (pH 2–10)
Decomposition	• With heat T > 90 °C (194 °F); • heating at pH < 3.5; • strong acids or alkali, strong oxidizing agents; • specific enzymes
Film formation	Low
Emulsion stabilization	Medium
Gelation	No (only with borate ions)
Gel strength and gel stability	—
Gel transparency	—
Tendency for gel synaeresis	—
Impact of electrolytes (cations +, 2+, 3+)	Addition of cations 2+ or 3+: viscosity increase
Reaction with Ca^{2+} ions	No (only viscosity increase)
Protein activity	No
Crystallization control	High
Synergistic effects with other hydrocolloids	+ Starch/xanthan/CMC: viscosity increase; + gelling polysaccharides (e.g. agar): increased gel strength and elasticity
Other synergistic effects	Gelation with borate ions
Negative interactions	Viscosity reduction with polyols
Dosage level in foods	Low to medium (0.05–2%, mostly 0.2–0.5%)

reduction and fibre enrichment. In beverages, the gum maintains turbidity (clouding effect) and solid suspension.

Toxicology and Regulatory Affairs

Animal studies have not shown negative interactions. Guar gum is a globally approved food additive (as E 412 in Europe). There is no ADI defined. In some

countries, guar is considered as food. The pods are cooked as vegetable for human consumption and are used as cattle feed. During passage through the digestive tract, the β-(1 → 4)-linkage of the main backbone is not cleaved, the α-(1 → 6)-linkages of the side chains are partially cleaved. Therefore, the water retention capability of guar is maintained. The gum is a soluble fibre with a strong retarding effect on the speed of glucose resorption. A positive effect on cholesterol level in the blood serum has been observed [1].

There are strongly depolymerized guar gum products, sold as food ingredients on the market, with molecular weights about 20 kDa. However, these do not meet the specifications of E 412 in Europe and have no E-number [2].

1.3.2 Locust Bean Gum (Carob)

Raw Material and Manufacturing

Carob gum or locust bean gum (LBG) is produced by milling the endosperm of the seeds of the carob tree (*Ceratonia siliqua*, family Leguminosae). The trees grow around the Mediterranean Sea and in California; 70–75% are found in Italy, Spain, Portugal, and Greece. It takes 8–10 years before the trees bear fruit called pods or St. John's bread. The pods are 10–20 cm long. The carob seeds or kernels are 8–15% of the pod's weight. Under normal weather conditions, about 280 000–300 000 tonnes of pods are collected manually each year. The pods are broken using a kibbling process, during which the seeds are released. The kibbled de-seeded pods are known as 'pulp' and finely ground pulp, also called carob powder, which is used as animal feed for all kinds of livestock, as a remedy against diarrhoea in children, and as raw material for alcohol production. Roasted pulp is also used as replacement for cocoa. The seeds consist of 30–33% hulls, 23–25% germs, and 42–46% endosperm. The hulls are either carbonized by hot sulfuric acid, followed by intensive washing with water, or largely removed by roasting in a rotating furnace at about 550 °C (1022 °F), after which residual hull fragments are rubbed off mechanically. The treated remnants of the seeds are then split and sifted. The recovered endosperm halves are dried and ground into a fine, off-white powder of desired particle size. The average annual production of food-grade gum is about 11 000 MT [1,2].

Chemical Structure

Carob gum contains (max.) 15% water (max.), 7% protein (max.), 4% acid insoluble residue (fibre) (max.), less than 1.2% ash, and a minimum of 75% polysaccharides (galactomannans). It is a neutral polysaccharide consisting of D-mannose and D-galactose in a molecular ratio between 73 : 27 and 86 : 14, with an average of 3.5 : 1 (Table 1.7). The molecule consists of a linear backbone of β-(1 → 4)-linked mannose units. Statistically nearly every fourth mannose molecule is bond to a galactose residue with an α-(1 → 6)-linkage. However, enzymatic hydrolysis has shown that the galactose residues are distributed irregularly within the mannose chain. There are zones with unsubstituted mannose blocks

Table 1.7 Characteristics of locust bean/carob gum.

	Locust bean gum/carob gum
E-No.	E 410
Origin	Extract of endosperm of seed (Leguminosae)
Chemical composition	• Low-galactose galactomannan; • mannose + galactose (ratio M : G = 3.5 : 1)
Nutritional value (in 100 g) – metabolism	252 kJ (60 kcal); slow resorption
Fibre content	Approx. 80% (contains 7% protein)
Toxicology	No health concerns, no ADI value defined
Solubility at low temperature (H_2O)	Limited soluble
Appearance of an aqueous solution	Opaque, grey, cloudy
Viscosity of solution in water	Low in cold water, high after heating + cooling
Impact of heat on viscosity in water (pH 7)	Viscosity increase of cold processed solutions, no heat thinning
Viscosity development in water at pH 7 (T = 0–100 °C)	High viscosity after heating and cooling
Shear stability	Pseudoplasticity (shear thinning)
Thickening effect	High, after heating to 80 °C (176 °F)
pH stability	High (pH 3–11)
Decomposition	• Heating at pH < 3.5; • strong acids or alkali, strong oxidizing agents; • specific enzymes
Film formation	Low
Emulsion stabilization	Medium
Gelation	Only with xanthan (optimum ratio at pH 7 = 1 : 1) or κ-carrageenan
Gel strength and gel stability	Stable thermoreversible gels with xanthan
Gel transparency	Low
Tendency for gel synaeresis	No synaeresis in gels with xanthan or κ-carrageenan
Impact of electrolytes (cations +, 2+, 3+)	Low
Reaction with Ca^{2+} ions	No
Protein activity	No
Crystallization control	High
Synergistic effects with other hydrocolloids	+ Xanthan: viscosity increase + gel formation + κ-carrageenan: increased gel formation (higher gel strength + elasticity, syneresis-free) + other gel formers (agar, alginate): increased gel strength and elasticity
Other synergistic effects	—
Negative interactions	—
Dosage level in foods	Low to medium (0.1–2%, mostly 0.2–0.5%)

and zones where two adjacent mannose units carry a galactose residue. The average molecular weight is about 310 kDa [1].

Solubility and Viscosity

Owing to its reduced amount of side chains compared to guar gum, LBG is not fully soluble in cold water. When heated to above 80 °C (176 °F), it is totally soluble and forms pseudoplastic solutions. Solutions heated to this temperature and cooled have a much higher viscosity than cold-prepared solutions. The viscosity is stable in a range of pH 3–11. Mono- and divalent cations only have a slight impact; the addition of anions usually has no effect.

Properties

The properties of LBG correspond substantially to those of guar gum so that both gums are used alternatives. Certain hot water-soluble fractions of LBG self-associate to form weak three-dimensional gel networks, especially after a freezing process.

LBG has the very important characteristic of being able to act synergistically with κ-carrageenan and xanthan to form gels that are elastic, very cohesive, and relatively free of synaeresis. LBG interacts more strongly with other polysaccharides than does guar gum. Evidence is accumulating that the interaction effects of LBG with hydrocolloids like cellulose, xanthan, κ-carrageenan, and agarose are due to direct molecular association between the two polymer types. The superior interactive properties of LBG are clearly linked to its lower degree of galactose substitution [2,3].

Applications

LBG is used in the same applications as guar gum and in all products where the synergistic gelation gives additional benefits (e.g. ice cream, sorbets, chilled dairy desserts). Water gels are made with LBG to be heated and form solutions to accompany prepared meat, fish and other seafood products. The low energy and high fibre content makes it suitable for healthy foods and products intended for diabetics.

Toxicology and Regulatory Affairs

Clinical trials with commercial LBG products did not show negative results on the human digestive tract and no allergenic reactions. In addition, animal studies did not show negative interactions. LBG is a globally approved as food additive (as E 410 in Europe). There is no ADI defined [1].

1.3.3 Tara Gum

Raw Material and Manufacturing

Tara gum, also known as Peruvian carob bean gum, is obtained by grinding the endosperm of the seeds of the South American tara tree *Caesalpinia spinosa*,

which belongs to the Leguminosae family. The trees grow at up to 3000 m above sea level in Peru and Bolivia and tolerate dry climate and poor soil conditions. The fruit is a flat oblong reddish pod that contains 4–7 large round black seeds composed of endosperm (22% by weight), germ (40%), and hull (38%). Mature pods are usually harvested by hand and typically sun dried before processing.

Based on seed weight, the yield of high-grade tara gum is only 21–22%.

However, the EU purity criteria specify a maximum limit for protein content of only 3.5% (N% × 5.7). This is significantly lower than the permitted maximum limits for carob/LBG (7%) or guar gum (10%). Thus, tara gum is clearly the purest seed gum. An estimated volume of 1500–2000 MT per year is available globally and is mainly used in the food industry. The purification principle is the same as for carob and locust bean gum (LBG) [2].

Chemical Structure

Tara gum is a neutral polysaccharide, a galactomannan, of high molecular weight. It consists of a linear main chain of β-(1 → 4)-linked D-mannose units that has side chains of α-(1 → 6)-linked galactose units. Statistically, each third mannose unit carries one galactose (M : G = 3 : 1) [1].

Solubility, Viscosity, and Stability

Tara gum is partially soluble in cold water (80% at 25 °C/77 °F) and it is completely soluble in hot water. The aqueous solutions are neutral. A solution of tara gum is less viscous than a guar gum solution of the same concentration, but more viscous than a solution of LBG. Generally, tara gum presents a viscosity of around 5500 cps (1% in water). Furthermore, tara gum shows an intermediate acid stability between LBG and guar gum. It resists the depolymerization effect of organic acids down to a pH of 3.5. This gum is also stable to high temperature heat treatment, up to 145 °C in a continuous process plant.

Properties

Tara gum is a white to yellowish powder. The properties are similar to those of guar and LBG. The addition of 60–70% sugar to a tara gum solution leads to weak gel formation. Xanthan causes a gelation of tara gum, too, but the gels are weaker than those of xanthan with LBG. More synergistic effects are found with agar and carrageenan, where tara gum supports gel formation.

Applications

Tara gums function mainly as a thickener and stabilizer in several food products. Blends with modified and unmodified starches can be produced that have enhanced stabilization and emulsification properties and are used in convenience foods, such as ice cream.

Toxicology and Regulatory Affairs

Tara gum is not digested by enzymes in the human body. Animal studies have not shown negative effects. In the USA, it is approved as a food additive by the

Food Chemicals Codex (FCC). In Europe, it is approved as hydrocolloid E 417. There is no specified ADI.

1.3.4 Tamarind Seed Gum

Raw Material and Manufacturing

The raw material for tamarind gum is the flour of tamarind seed. These seeds grow on the tamarind tree (*Tamarindus indicus*, family of Leguminosae), one of the most important and popular trees in India. Tamarind seed flour is extracted by cooking it for 30–40 min with boiling water (30–40 vol.%) under stirring. The water contains 0.2% organic acid. The extract is left overnight and insoluble material is removed by filtration. 0.5% Kieselguhr is added to the remaining liquid and pressure filtration performed. The filtrate is dried under vacuum and precipitated by ethanol. Tamarind gum is a creamy-white powder without taste and odour [1].

It is the only seed xyloglucan that is exploited commercially [3].

Chemical Composition

Besides polysaccharides, tamarind gum contains about 15% water, 3% protein, 1% fibre, and small amounts of phosphate and oil. Building blocks of the polysaccharide are D-glucose, D-galactose, and D-xylose in the ratio 3 : 1 : 2. L-Arabinose is also present in smaller portions. The macromolecule consists of a linear main chain of β-(1 → 4) linked glucose units. Side chains bond at the 6-position are xyloses, arabinoses, and galactose with different chain lengths. The average molecular weight is 50–115 kDa.

Properties

The characteristic property of tamarind gum is its capability to form stable gels with sugar at 0.5–1.5% gum concentration in water. These gels are stable over a wide pH range. The sugar concentration required to form a specific gel strength is lower than for pectin. The gels do not tend to show phase separation (synaeresis). With 45–70% sugar, the gum forms heat- and pH-stable gels with very high gel strength. Sugar can be partially replaced by alcohol (up to 20%). The maximum gel strength for a gel with 1% gum and 50% sugar is at pH 2.8.

Application

Owing to this gelation behaviour, tamarind gum can replace pectin in fruit preparations, jams, and marmalades. Another application field is ice cream and mayonnaise-type products.

Toxicology and Regulatory Affairs

Tamarind gum is used traditionally in Japan to produce jams, jellies, dressing, and ice cream. Tests have not shown negative effects on animals.

In Europe and the USA the use of tamarind gum has lapsed and it does not currently have clearance for use food use [3].

1.3.5
Konjac Gum

Raw Material Origin and Manufacturing

Konjac flour was known in China as long ago as 200 BC. It yields a high molecular weight viscous polysaccharide – konjac glucomannan. The flour is obtained from the tubers of less than ten species of *Amorphophallus*. Most species have a glucomannan concentration of more than 50% (dry matter). The size and shape of tubers depend on age and cultivar (diameters of 15–20 cm are frequent). Mainly, 3-year-old tubers 0.3–1.5 kg in weight are washed and peeled before being sliced into chips. The characteristic smell of konjac may be washed out along with other alcohol-soluble ingredients by a 10–50% alcohol solution to give a cleaner odour and taste. Processing steps are dry and semi-wet milling to increase the concentration of glucomannan. The polysaccharide precipitates when organic solvent is added [2].

Chemical Structure

Konjac glucomannan is mainly composed of a backbone of β-(1 → 4)-linked D-glucopyranose and β-D-mannopyranose sugars in a random order. The molecular ratio of mannose to glucose is on average 1.6 : 1 and is random, though small repeats of three to five mannose blocks are frequent. Randomly spread acetyl groups occur every 10–19 units (3–6%) on carbon atoms C2, C3, or C6 of mannopyranose. Methylation and carboxylation, as well as single sugar substituents or longer side chains, have been documented. Although derivatization improves chain flexibility, these products are not permitted for food use. The average molecular weight is 1 MDa. Commercial products range between 200 000 and 2 million daltons [2].

Solubility and Viscosity

Konjac flours even solubilize in ice water. Hydration is accelerated by raising the temperature and speed of agitation. Viscosity and solubility can be hindered by addition of competing solutes, low-molecular-weight ingredients or maltodextrin, branched dextrins, and salts. Alcohols, such as ethanol or isopropyl alcohol, also reduce solubility and can eventually precipitate the glucomannan chains out of solution. Konjac flours have a remarkable absorption capacity and can absorb 15–20 g of water or 1–2 g of oil per g. Increased acetylation levels reduce the water absorbency and viscosity. The gum is degraded by prolonged exposure above 80 °C (176 °F), especially in acidic media. Konjac solutions are sensitive to shear-thinning. High-purity galactomannans are difficult to solubilize. Konjac exhibits high viscosity solutions at 1%, but it is much less viscous than guar or xanthan gum at lower concentrations. Extreme values of konjac for molecular weight and viscosity could be linked to the presence of microgel particles, so-called clusters, produced during processing. Native konjac material, crude flour, is still bound to the original protein membrane, which must swell first before the

konjac molecules are released into solution. Viscosity is positively correlated with glucomannan content and degradation of chain length reduces it. Solutions of native grades exhibit non-Newtonian flow behaviour and shear-dependant viscosity. Preservatives should be used to prolong the shelf life of gel and stock solutions [2].

Properties

The less-substituted konjac glucomannan has a stronger interaction effect than locust bean gum because the unsubstituted mannan backbone segments are critical for forming interchain associations [3].

Eliminating acetyl groups produces deacetylated konjac glucomannan, which is able to build random junction zones through hydrogen bonds to form an irreversible and extremely stable gel with similar elastic recovery to polyacrylamide gels. Acidic deacetylation is possible, but alkali reactions are preferred to limit hydrolysis. In some cases, temperature-stable gels may be obtained without deacetylation. Non-modified konjac flours show different gelling properties depending on pH, concentration of other ingredients, and presence of synergistic hydrocolloids, such as semi-refined, κ- or ι-carrageenan, or xanthan gum. With those, konjac forms elastic, cohesive gels. Maximum peak viscosity is achieved with a blend of 75–90% konjac and 10–25% carrageenan. For milk gels with ι-carrageenan, the maximum gel strength is obtained with a 20 : 80 to 40 : 60 blend of konjac flour to carrageenan. In brines, konjac is only used in low levels to boost carrageenan gel strength and reduce thickening power. A blend of xanthan (50%) and konjac (50%) with a total gum concentration of 0.02% gives a very elastic thermoreversible gel. Xanthan shows more affinity for glucomannan than the galactomannans (LBG, tara gum). A konjac–xanthan blend is more influenced by salts than a LBG–xanthan blend. With 0.04 mol l^{-1} NaCl, xanthan gels konjac glucomannan already at 42 °C (107 °F). Konjac improves the functional properties of starch (viscosity, freeze–thaw stability) and reduces synaeresis. Gels of 1% konjac and 9% starch are thermoirreversible and very acid stable. Konjac improves the gel strength of agar when added in a ratio of 10% to 90% agar. Long-chain konjac glucomannan can influence gellan gum gelation promoted by salts. High concentrations of konjac glucomannan (2–5%) may gel without any additive. These gels are not clear and do not exhibit a specific fusion temperature. Glucomannan has affinity for iron, zinc, calcium, and magnesium salts – high amounts of glucomannan can reduce the mineral intake because of physical entrapment. Lyotropic salts alter the gel properties.

Some grades show suspension activity. Sheared konjac gels have an oily creamy mouthfeel [2].

Applications

Konjac is used for shelf-life extension in bakery products at 0.1–0.5%. It provides adhesion for coatings and binding in complex matrixes such as restructured

meat or vegetable products, pasta, and desserts. Often, konjac is blended with xanthan, carrageenan, or starches. The gum is used to thicken fluids for patients with dysphagia [2].

It is used as vegan substitute for gelatine. Konjac root powder is used as an ingredient in vegan alternatives to seafood products. It can be incorporated into animal product-free versions of scallops, fish, prawns, crab, and shrimps.

Toxicology and Regulatory Affairs

Konjac glucomannan is sensitive to enzymes such as β-D-glucanase and β-D-mannanase and thus bacterial fermentation is able to occur in the intestines.

Konjac lowers cholesterol level more effectively than other gums and it regulates the blood sugar level. It synergistically acts with stanols and sterols for low-density lipoprotein (LDL) reduction. Konjac acts as prebiotic in the human colon. It has low energy content and reduces appetite. It is a globally accepted gelling agent and thickener. It has a substantial record as a common healthy ingredient in Asia. In Europe it is approved as E 425 with a maximum intake of $10\,g\,kg^{-1}$ food [2].

1.4 Exudates

1.4.1 Acacia Gum/Gum Arabic

Raw Material Origin, Quality, and Purification

Acacia gum, also known as gum Arabic, is a natural gum exudate obtained from acacia trees in the 'African sub-Saharan zone' from 12 different countries, from Senegal to Ethiopia, the so-called gum belt. It has been known since antiquity and used for thousands of years as food additive and ingredient. The FAO/WHO has defined acacia gum as the dried exudate obtained from the stems and branches of *Acacia senegal* or *Acacia seyal* (family Leguminosae). The gum occurs as resinous mass naturally or is secreted through artificial cuts made from December to May. One tree produces only about 400 g of gum per year. Within a few weeks, the exudate dries to tubers and sheds in sunlight. These are collected, cleaned of the rest of bark and, depending on colour, sorted into different quality classes. Raw gum has several vegetable and mineral impurities and fluctuating bacterial contamination. Using dry purification steps such as sieving only, the level of impurities can be reduced but microbial contamination cannot be improved and, most of the time, raw gum does not meet international requirements for foods. Consequently, dry methods of purification have been substituted by purification in aqueous solutions, which is much more efficient. The gum is fully dissolved in water and all impurities are removed by a cascade of filtration steps giving levels of

insoluble matter in the finished products as low as 0.02%. Bacteriological contamination is reduced by pasteurization and the gum syrup is concentrated to 25–35% and dried. During solubilization, purification, and drying the thermal conditions are critical. Acacia gum contains proteins that are very important for the emulsifying properties but are sensitive to heat denaturation. Roller drying gives gum powders with good hydration properties, but less emulsifying capability due to the drastic thermal treatment. By spray-drying, highly functional fine powders are obtained. Recently, multistage drying processes have been developed to produce agglomerated gum particles with unique dissolution in water without lump formation and with a maximum solubility of 45–50%. The fine-to-coarse powders are off-white to yellowish. Exudates of other plants (e.g. *Combretum* species) are falsely offered as gum Arabic. The consumption of acacia gum from *A. seyal*, restricted to technical applications in the past, is now about the same as from *A. senegal*. With more than 60 000 MT, it is the third largest hydrocolloid additive used by industry [1,2].

Chemical Structure

Acacia gum is a highly branched neutral to slightly acidic complex polysaccharide (Table 1.8). Building blocks of the arabinogalactan macromolecule are D-galactose, L-arabinose, L-rhamnose, and D-glucuronic acid in a molecular ratio of about 3 : 3 : 1 : 1. The structure consists of a linear backbone of β-(1 → 3) linked galactose units that has side chains of α- or β-(1 → 6) linked galactose units with a terminal glucuronic acid group. The acid groups are partially neutralized by calcium, magnesium, sodium, or potassium ions and occur partially in a free-acid form. The side chains are further branched with rhamnose or arabinose units. The arabinogalactan chains are attached to a protein skeleton forming an arabino-galactoprotein (AGP). Depending on source, acacia gum has different compositions. A simple test to identify the gum source is the specific rotation (*A. senegal* = −30°; *A. seyal* = +51°). For further structural information, sugar composition is determined by HPLC after acidic gum hydrolysis. The nitrogen content of *A. senegal* (0.29%) is about double that of *A. seyal* (0.14%). The lower content of protein combined with a lower protein availability explains why *A. seyal* is less efficient for emulsion stabilization and, consequently, it is not used for emulsions where long-term stability is required. The molecular weight varies within wide limits and is on average 350 kDa [1,2].

Solubility and Viscosity

Acacia gum powder hydrates readily in cold water and concentrations up to 40–50% can be handled easily. Compared to other water-soluble polysaccharides with a similar molecular weight, acacia gum exhibits very low viscosity in water. To reach a viscosity of 3000–5000 mPa s (Brookfield), only 1% of guar or xanthan gum is necessary, but acacia gum has to be dissolved at concentrations of 40–45%. Rheological behaviour of acacia gum solutions is Newtonian up to 25% and then becomes pseudoplastic. Highly concentrated solutions exhibit only a slight shear-thinning. The aqueous solutions have an acidic character (pK_a 4.5–5.5).

Table 1.8 Characteristics of acacia gum/gum Arabic.

	Acacia gum – gum Arabic
E-No.	E 414
Origin	Exudate of a tree (Acacia)
Chemical composition	• Highly-branched arabinogalactan; • galactose, arabinose, rhamnose, glucuronic acid in a molecular ratio of 3 : 3 : 1 : 1
Nutritional value (in 100 g) – Metabolism	837 kJ (200 kcal); slow resorption
Fibre content	High (contains 80% starch/sugar)
Toxicology	No health concerns, no ADI value defined
Solubility at low temperature (H_2O)	100% cold-water soluble (solutions possible with 40–50% concentration)
Appearance of an aqueous solution	Grey-white to yellowish
Viscosity of solution in water	Very low in cold water (natural pH about 4–5), viscosity is further reduced upon heating
Impact of heat on viscosity in water (pH 7)	Slight viscosity decrease – fully reversible at pH 4–9
Viscosity development in water at pH 7 ($T = 0$–$100\,°C$)	Slight viscosity decrease upon heating
Shear stability	Newtonian $\leq 25\%$, pseudoplastic $> 25\%$
Thickening effect	Low, very high concentrations necessary
pH stability	Medium (pH 4–9)
Decomposition	By strong acids or alkali ($4 > pH > 9$), but extremely heat- and enzyme-stable
Film formation	High
Emulsion stabilization	High
Gelation	—
Gel strength and gel stability	—
Gel transparency	—
Tendency for gel synaeresis	—
Impact of electrolytes (cations +, 2+, 3+)	Precipitation + viscosity reduction (e.g. $CaCl_2$)
Reaction with Ca^{2+} ions	Precipitation + viscosity reduction (e.g. $CaCl_2$)
Protein activity	No
Crystallization control	Low
Synergistic effects with other hydrocolloids	—
Other synergistic effects	• Interaction with sugar and sugar alcohols; • complex formation with sodium citrate (viscosity increase)
Negative interactions	• Coacervate formation with gelatine + precipitation; • electrolytes reduce solution viscosity
Dosage level in foods	High (in most cases >5%)

The presence of uronic acids in acid and salt forms makes the viscosity of solutions dependent on pH value and electrolyte content. However, it also gives acacia gum buffer properties so that solutions are more pH stable after moderate addition of acids or bases. Viscosity has a broad maximum at pH 4.5–7 and is stable in a pH range of 4–9. Degradation occurs in stronger acidic or alkaline conditions, whereby viscosity decreases irreversibly (50% loss at pH 2 or pH 12). The addition of electrolytes results in a decrease in viscosity. An exception is sodium citrate, which increases solution viscosity due to complex formation. Acacia gum can be dissolved in hot ethylene glycol or glycerol as well as in aqueous ethanol solutions of up to 60 vol.% alcohol. Viscosity decreases upon ageing, but this effect can be minimized by addition of preservatives such as benzoic acid (0.2%). Normal mechanical treatment has no effect on viscosity. Prolonged exposure to ultrasonic vibration or ultraviolet irradiation reduces viscosity. The highly branched structure makes it highly resistant to hydrolysis in medium-acidic systems and to degradation under extreme thermal conditions and by enzymes [1–3].

Properties

The highly branched compact arabinogalactan structure is responsible for the low viscosity of solutions while the central protein fraction provides good emulsification properties, especially when using grades from *A. senegal*. The emulsifying power is lost upon heating, which causes some precipitation of proteinaceous material. It is the high molecular mass protein-rich fraction that preferentially adsorbs at the oil–water interface. In confectionary products, acacia gum in high concentrations (>40%) interacts with sugar, also present in high amounts, thereby preventing its crystallization and giving smooth products of uniform texture. A similar strong interaction occurs between the gum and polyols (sorbitol, mannitol) that replace sugar in dietetic hard candies. Corn starch and maltodextrins, which are ingredients of chewy or hard sweets, are prevented from aggregating. The gum (1%) offers a long-lasting, cohesive chew in chewy confectionary. Furthermore, it stabilizes the fats in caramels and toffees. The film-forming ability is high [2,3].

Applications

Acacia gum is used as an emulsifier and stabilizer in a range of confectionary products. It stabilizes flavoured oil emulsions and is often found in beverages. In tablets, it is used as binder. It improves the quality of soft and hard coatings for food, nutraceutical, and pharmaceutical products. Acacia gum is used for effective encapsulation – as emulsifier as part of the matrix or as coacervate partner in membrane encapsulation.

It brings benefits to bakery products in terms of processing, texture, and shelf life due to its moisture regulation and film-forming properties. The gum is used as traditional oenological additive to protect red and white wine against destabilization (10–30 g per 100 l). In health foods it is a source of soluble fibre with prebiotic properties and lowers the glycemic index by reducing the speed of sugar resorption [2,3].

Toxicology and Regulatory Affairs

Acacia gum resists digestion in the stomach and the small intestine. However, it is slowly fermented by the microflora colonizing the gastrointestinal system. Resorption occurs in the large bowel after synthesizing short-chain fatty acids. The gum has prebiotic function and promotes selectively the beneficial bacteria from the lactic acid group. The gut tolerance is high; there is no gas production and no laxative effect. It has a hypoglycaemic effect and reduces GI at concentrations of 3–6%. It is a non-carcinogenic polysaccharide.

Acacia gum is approved by the US FDA and has GRAS status. In Europe, it is classified as E 414 as food additive for technological purposes in unrestricted dosage ('quantum satis'). The calorific value is $2\,\mathrm{kcal\,g^{-1}}$ (Europe). The gum is globally approved for pharmaceutical applications and it is listed in the US National Formulary and European Pharmacopeia [2,3].

1.4.2 Tragacanth

Raw Material Origin, Harvesting, and Quality

Tragacanth is mentioned in the Bible. It is the exudate from the trunk and branches of the shrubby representatives of the species *Astragalus* (family Leguminosae). The two main commercially exploited species are grown predominantly in Iran, Syria, and Turkey. Approximately 1000 MT per annum where used in 1980, then demand fell to about 300 MT. It was replaced by new xanthan grades and the Gulf War made tragacanth supply erratic.

Longitudinal incisions are made with a knife into the lower stem of the shrubs in May or June. Collection of the exudate occurs in the hot summer months for the high-quality ribbon grades and later for the flake grades. Collected material is hand-sorted according to colour and viscosity. It is exported mainly to Europe and USA where further processing steps – such as grinding down to 150 µm particle sizes and selective sieving – are carried out. Blends are made to ensure consistent quality of this natural product [2].

Unground tragacanth is a white to yellowish, transparent, horn-like material 0.5–2.5 mm thick. Milled products are white or off-white powders.

Chemical Structure

Gum tragacanth can be described as a complex, acidic, highly branched, heterogeneous hydrophilic polysaccharide. The molecular weight is about 840 kDa. Tragacanth is a mixture of two components present as a mixed calcium, magnesium, and potassium salt. The first component is tragacanthic acid, commonly known as bassorin, a water-swellable polymer (60–70%).

The second component is a water-soluble arabinogalactan polysaccharide, known as tragacanthin (30–40%). It is made of 75% L-arabinose, 10% D-galactose, and 10% D-galacturonic acid which is esterified with methanol. The structure is believed to consist of a core of repeating (1 → 6)-linked D-galactose units to

which highly branched chains of L-arabinofuranose residues are attached. Traces of starch and cellulosic materials are present and the proteins (3–4%) contribute to the emulsification properties of the gum.

The water-swellable tragacanthic acid yields D-xylose, L-fucose, D-galactose, L-rhamnose, and D-galacturonic acid. The viscous property of the gum is largely due to this component having a high molecular weight and rod-like molecular shape as it has a (1 → 4)-linked D-galactose backbone with short side chains of D-xylose, L-fucose, or D-galactose connected by (1 → 3)-linkages [2].

The tragacanthic acid fraction occurs associated with Ca^{2+}, Mg^{2+}, and K^{+} [3].

Solubility and Viscosity

Gum tragacanth hydrates in hot or cold water to form viscous solutions. Tragacanthin dissolves in water to form a colloidal solution, while bassorin forms a gel. Gelation properties of this fraction are improved by Ca^{2+} ions. Viscosity depends on the grade and is regarded as the main indicator for quality. Viscosity is fully developed after 24 h at 25 °C (77 °F). The hydration time can be reduced as the initial water temperature is increased (e.g.: 2 h at 50 °C (122 °F)). Tragacanth solutions are pseudoplastic at concentrations as low as 0.5%. Aqueous dispersions containing more than 2% of gum form thick pastes that have the texture of soft gels [2,3].

Properties

The gum is stable over the pH range 2.5–10; the highest stability is between pH 4 and 8. The pH of a 1% solution is acidic (pH 4.5–6). Viscosity decreases by only 30% as the pH falls to 2. This unusual stability under acidic conditions (~20% viscosity loss only when 1% gum is stored in 1% acetic acid for 3 weeks) was the reason for the extensive use of gum tragacanth in foods such as salad dressing and acidified sauces, where maintenance of viscosity at low pH is required. Heating leads to a reversible decrease in viscosity by about 25–50% during heating from 25 to 90 °C (77–194 °F) – upon cooling the initial thickening effect is almost fully recovered. Permanent viscosity loss will occur during prolonged heating at elevated temperature or if heat is applied during hydration. Then an irreversible viscosity loss (about one-third) occurs that is ascribed to autohydrolysis. Gum tragacanth is an effective bifunctional emulsifier that lowers the interfacial tension between oil and water. The minimum surface and interfacial tension is reached at a gum concentration of only 0.25%. Tragacanth is compatible with most hydrocolloids, proteins, and fats used in food preparation. However, interaction with acacia gum results in a viscosity reduction and improved emulsifying properties of the mixture. This reaction is exploited to produce pourable emulsions with long shelf life. Pure gum solutions are unusually stable to microbial attack and have long shelf lives without loss of viscosity [2,3].

Applications

Many of the traditional tragacanth applications now use more cost-effective additives such as xanthan gum, but it is still used where the viscosity properties, emulsifying ability, and acid stability are superior to other food hydrocolloids [2].

Tragacanth is used as filler, stabilizer, emulsifier, thickener, or gelling agent in icings, confectionary, salad dressings, sauces, ice creams and sherbets, bakery fillings, and oil emulsions. In beverages, it suspends the pulp, prevents settling of fruit particles, and gives the desired body.

Toxicology and Regulatory Affairs

The US FCC classifies tragacanth as GRAS. There is no ADI specified from WHO/FAO. The Scientific Committee of Food (SCF) in Europe lists it in Annex I of the 'Directive for food additives other than colours and sweeteners' – with unrestricted dosage (quantum satis). Although allergenic responses have been reported from animal studies, it is not listed in the European allergen list (Annex IIIa) [2].

1.4.3
Karaya Gum

Raw Material Origin, Harvesting, and Quality

Gum karaya, also known as sterculia gum, India gum, or Indian tragacanth, is a dried tree exudate obtained from certain species of *Sterculia* (*Sterculia urens* and other species, family Sterculiaceae) or from *Cochlospermum* species (family Bixaceae). The gum is obtained by making incisions into the trunks. The gum exudes within 24 h in large irregular lumps or tears that dry in the hot climate. Each tapping yields between 1 to 5 kg of gum and each tree can be tapped about five times during its life time. The Indian crop is harvested between April and June, before the monsoon season. The crop in Senegal is collected in September to January or from March to June. The gum is collected in bigger volumes. Then bark and foreign matter (BFM) are removed by hand. Lumps are broken down into smaller pieces. Sorting occurs on the basis of gum colour and residual BFM. Premium quality superior no. 1 is used for food and pharmaceutical applications and may only contain 0.5% BFM. It gives light-coloured solutions and high viscosities. As BFM increases, the solution colour becomes darker. Technical grades contain more than 3% BFM. Further processing is carried out in Europe and USA. The gum is mechanically ground to particle sizes below 110 µm. Fibres, bark, and other foreign material are removed by aspiration and density-table separation. Blending is an option to obtain products with consistent colourizing and thickening effect [2].

The demand for highly-purified gum karaya has decreased from approximately 6000 MT globally in the early 1980s to 3000 MT in 2010. The shift has been towards more cost-effective gums. India is the biggest producer (50–70%), with the remaining volume produced in North Africa. Some 75–80% of the crop is imported by the USA.

Chemical Structure

Gum karaya is a complex, branched, acid polysaccharide composed of the building blocks D-galactose, L-rhamnose, D-galacturonic, and L-glucuronic acid. The gum naturally occurs with Ca^{2+} and Mg^{2+} ions associated with the uronic acid groups. The amount of uronic acid is about 37%. The L-rhamnose content is much higher compared to other exudate gums – this can be used for identification. The monosaccharides are partially acetylated. The molecule contains 8–14% acetyl groups (dry matter basis), depending on karaya source and its age. Free acetic acid is split off on ageing. Increased temperature and humidity and fine particle size increase the rate of acetic acid formation. The structure of karaya contains a central chain of galactose, rhamnose, and galacturonic residues with side chains of glucuronic acid. The exudate occurs as a mixed calcium and magnesium salt. Approximately 1% proteinaceous material has been detected. The average molecular weight is extremely high and is about 9.5 MDa; it can be up to 16 MDa [2].

Karaya can vary widely in its chemical composition, corresponding to which are several different compositions that are summarized below.

Solubility and Viscosity

Because of the presence of acetyl groups and the strong crosslinking, gum karaya is the least soluble of the commercial exudates. It swells in water, to many times its original volume, without dissolution. It does not dissolve in water to give a clear solution but absorbs cold water rapidly to form viscous colloidal dispersions at low concentrations (<0.02% in cold water, 0.06% in hot). At high concentrations of 3–5%, the gum forms thick, soft gel-like pastes that have spreadable quality and are ideal for suspending particles. Karaya solutions exhibit true plasticity at 2–3% as a consequence of the high degree of ordered structure and its large, heavily branched molecular network, which absorbs and immobilizes water very strongly and therefore offers considerable resistance to flow. Hydration depends on particle size – finer gums hydrate much more rapidly than coarser gums. Application of high shear to grainy dispersions from coarse powders will give smooth solutions with reduced viscosity. Heating increases solubility, due to a change in the polymer conformation, but results in a permanent viscosity loss. A maximum of up to 4% gum can be hydrated in water. By heating under pressure, colloidal solutions with 20% concentration can be produced. The viscosity decreases with increasing age of the powder. Grinding to fine particles reduces viscosity, too. High storage humidity or high storage temperatures also contribute to viscosity loss. Boiling gum solutions for more than 2 min leads to an irreversible viscosity reduction. The solutions show thixotropic flow behaviour. The viscosity depends strongly on pH. The pH of a 1% solution is about 4.6. Above pH 7, alkali irreversibly transforms the characteristics of short-bodied karaya solution into a ropy, stringy mucilage with a ninefold increase in viscosity. This has been ascribed to irreversible deacetylation of the karaya molecule. The maximum viscosity occurs at pH 5–7. At

pH 2–5 and above 11, there is a strong viscosity decrease. Karaya forms viscous solutions in 60 vol.% alcohol, but is insoluble in higher concentrations of alcohol. The viscosity of karaya solutions remains constant for several days. Since these solutions are subject to microbial attack, preservatives are recommended. Depending on the food formulation benzoic or sorbic acid, methyl and propyl *para*-hydroxybenzoate, glycerol, and propylene glycol are commonly used [2,3].

Properties

Karaya has an acetic odour and taste. Its powder is light grey to pinkish grey. Cost is based on colour and purity. There is no distinct correlation between viscosity and grade. Where viscosity is important, the powdered karaya should be used within six months after processing, because its viscosity decreases with age.

Karaya is compatible with most other gums, as well as proteins and carbohydrates.

Interactions with sodium alginate have been reported to modify solution properties. Karaya reduces the gel strength of agar gels. Pyrilamine maleate, a strong hydrotrope and antihistaminic, and karaya are incompatible. Karaya dispersions lose viscosity when certain strong electrolytes (e.g. $CaCl_2$) are added in small amounts. Alkali and alkaline conditions make karaya solutions very ropy.

Applications

Karaya has similar physical characteristics to gum tragacanth and can replace it in some applications. The elimination of acetic acid restricts its use due to sensory reasons (odour, taste). The relatively good acid stability and strong water binding capability makes it suitable as a thickener and emulsifier in foods, as a bulk laxative, and adhesive for dentures or colostomy bags in medical and pharmaceutical applications.

Gum karaya is used as suspending aid and emulsifier in cold-processed dressings and sauces. Other application fields are aerated dairy desserts, cream, beer, and meringues where it stabilizes the foam. The gum prevents whey separation in cheese spreads, acts as binder in meat products, extends shelf life of baked goods, prevents synaeresis in gels, and controls ice crystal growth in sherbets, sorbets, and ice lollies. It is added as fibre source for dietary supplements – often in combination with guar.

Toxicology and Regulatory Affairs

Karaya gum is digested only to a minor extent, if at all [3]. It is classified in the USA as 'generally recognized as safe' (GRAS). The WHO/FAO did not specify an ADI. Within the EU, karaya is listed as E 416. In the past, the SCF of the EU set an ADI of 12.5 mg per kg body weight per day and allocated it to Annex IV of the 'Directive for food additives other than colours and sweeteners'. This legislation restricts karaya use to special food groups such as chewing gum, dietary food supplements, desserts, emulsified sauces, cereal and potato based snacks, egg-based liqueurs, bakery filling, toppings, and coatings [2].

1.4.4
Ghatti Gum

Raw Material Origin, Harvesting, and Quality

Gum ghatti is the dried exudate from the bark of the tree *Anogeissus latifolia* of the family Combretaceae. The tree is quite large and found in large numbers in the dry, deciduous forests of India and Sri Lanka. The crude gum has a glossy fracture and occurs in rounded tears, which are normally less than 1 cm in diameter. The bigger pieces are the size of a hazelnut. The colour of the gum exudates varies from off-white to dark brown. The lighter the colour, the better the quality. Crude ghatti has up to 15% total impurities at maximum 15% water. Since ghatti and karaya are found in the same geographic areas, the harvesting and grading are similar. The best crops are picked outside of the monsoon season, and the largest crop is harvested in April. After picking the gum, it is dried in the sun for several days. It is then hand sorted according to colour and impurities into various grades. There are also white commercial powder grades available, which are highly purified and spray-dried.

Chemical Structure

Ghatti gum is a water-soluble calcium–magnesium salt of a complex acidic polysaccharide. The monomers are L-arabinose (47.6%), D-galactose (28.6%), D-mannose (9.5%), D-xylose (4.8%), and D-glucuronic acid (9.5%). The molecular ratio is 10 : 6 : 2 : 1 : 2. Traces of rhamnose are found, too. The sugar components are partially acetylated (5.5% on dry matter). Three different structural elements are detected. The macromolecule consists of several main chains from β-(1 → 6) linked galactoses bonded to arabinose at the 3-position or to (1 → 4) linked glucuronic acid, as well as α-(1 → 2) linked mannoses bonded to glucuronic acid at the (1 → 4) position. In the 3-position to galactoses, there are side chains with arabinose and xylose units. The average molecular weight is 270 kDa. The molecules may have an overall rod shape in solution [1,3].

Solubility, Viscosity, and Properties

Gum Ghatti is 80–90% soluble in water. It can be dispersed in hot or cold water to form colloidal dispersions. Because of this limited solubility it is impossible to attain the concentrations reached with acacia gum. The viscosity of dispersion is very variable from one batch of gum to another – for example, the viscosity of a 5% dispersion of the best grade of gum ghatti varies between 30 and 400 mPa s. This has been ascribed to the presence of two different fractions in the gum, one soluble in cold water, the other forming a dispersible gel. Viscosity in water is controlled by the proportion of the latter, which is 10–30 times more viscous than the soluble fraction. The gelling component occurs in amounts of 8–25% and can be dissolved to some extent (~20% of the total) by stirring the gum at 92 °C (197 °F) for about 2 h, but complete dissolution requires maceration. The two fractions of the heterogeneous gum molecules differ in chemical and physical properties. Both fractions are largely in salt form with less than 10% of free acid.

The significant difference lies in the proportion of the different cations present: the soluble fraction contains about 62% Ca^{2+}, 32% K^{+}, 5% Mg^{2+} and 1% Na^{+}. In contrast, the dispersible gel fraction has a large Ca^{2+} content (>90%), 4% Mg^{2+}, 2% K^{+}, and no Na^{+}. The higher viscosity and lower solubility of the gelling fraction are due to aggregation, through interaction between the divalent Ca^{2+} ion and anionic groups on different molecules. Removal of Ca^{2+}, by precipitation with sodium carbonate, reduces the viscosity of gum dispersions irreversibly. This effect is not reversed on subsequent addition of Ca^{2+} which, conversely to alginates and other gums, further decreases viscosity. The effects of other cations, and of pH, on viscosity of gum ghatti dispersions differ little from those observed with acacia gum. The addition of sodium salts decreases viscosity. Ghatti dispersions are not affected by small amounts of acid or alkali since the gum acts as a buffer and reverts to its normal pH of about 4.8. The finer the particle size of the powdered gum, the faster it will swell and reach its maximum viscosity. If the gum is coarser than 150 mesh, solutions will be grainy and require a longer hydration time. Gum ghatti will not form a true gel. The dispersions are slightly coloured due to traces of pigments. The viscosity is a function of pH value. The optimum of viscosity is at pH 5–8, but stability is found from pH 3 to 11. At 3–5% gum concentration, a highly viscous (100–500 mPa s) dispersion of uniform smoothness and texture results. The dispersions are non-Newtonian – viscosity increases geometrically with concentration. Solution viscosity increases with time (about 10% every 7 days). The molecule is more resistant to glycosidic fission than acacia gum. Its viscosity is greater than that of acacia gum, but less than that of gum karaya [3].

The gum tastes mild and it is almost odourless. The colour of commercial powders varies from tawny to dark brown. The lightest colour has the least impurities and the greatest effectiveness in most applications. Ghatti is compatible with other plant hydrocolloids as well as carbohydrates, most proteins, and some fats. Viscosity loss is noted below pH 3 and above pH 11. A higher apparent viscosity is observed in an aqueous ghatti gum dispersion containing 25% ethanol. Dry films are relatively soluble and brittle. Ghatti has good emulsifying properties in particular for oil-in-water emulsions. To prevent bacterial attack in solutions, the gum is preserved with methyl and propyl *para*-hydroxybenzoate (0.15–0.02%), glycerine, or propylene glycol.

Applications and Regulatory Affairs

Gum ghatti has GRAS status from US FDA. In Europe it is not classified as a food additive. The world tonnage is relatively low. In general, applications are the same as for acacia gum. The stabilization of suspensions and emulsions is the most important use. In food, gum ghatti stabilizes butter-containing table syrups. It is used at about 0.4% in combination with 0.08% lecithin. Ghatti modifies the refractive index of table syrup until the syrup becomes clear. In pharmaceuticals and cosmetics, the gum is used to prepare stable, powdered, oil-soluble vitamins. It acts as a stabilizer in oil-in-water emulsions and in X-ray suspensions with barium sulfate.

1.5
Bacterial Polysaccharides

1.5.1
Xanthan

Raw Material and Manufacturing

Xanthan gum was first discovered in the 1960s and commercialized in the 1970s. It is produced by aerobic fermentation of glucose or sucrose solutions with pure cultures of *Xanthomonas campestris* or *phaseoli*. Owing to the high viscosity of the formed xanthan gum, the sugar concentration of the substrate may not exceed 5%. Commercial production is carried out batchwise by submerged fermentation with strong agitation. Besides the carbohydrates, the sterile medium contains a nitrogen source (yeasts) as well as nutrient and buffer salts like magnesium sulfate and other trace minerals. After initial inoculation with the selected strain, fermentation is continued for approximately 3 days at 30 °C (86 °F). At the end of the fermentation, the broth undergoes sterilization treatment to eliminate any viable microorganisms. The cellular components are removed by centrifugation. The xanthan gum is then recovered by precipitation with isopropyl alcohol. After separation of the fibres by centrifugation or filtration, they are dried and milled before packaging. Annual production is approximately 50 000 MT, 50% of which is used in food applications.

Xanthan gum is sold as an off-white powder with a moisture content of about 11% and ash content of 6–9% [2].

Chemical Structure

Xanthan is a long-chain polysaccharide with a high number of trisaccharide sidechains. The building blocks D-glucose, D-mannose, and D-glucuronic acid occur in a molecular ratio of about 3 : 3 : 2 (Table 1.9). The primary structure of xanthan consists of a cellulosic backbone of β-(1 → 4) linked D-glucose units substituted on alternate glucose residues with a trisaccharide side chain. The trisaccharide chain is composed of two mannose units separated by a glucuronic acid. Approximately half the terminal mannose units are linked to a pyruvate group (about 3.5%) and the non-terminal residue usually carries an acetyl group (about 4.7%). The carboxyl groups on the side chains render the molecules anionic. Xanthan gum has an average molecular weight of about 2000 kDa with a narrow-molecular-weight distribution compared to most polysaccharides [2].

Solubility, Viscosity, and Properties

Xanthan gum is a fast-hydrating water-soluble hydrocolloid that can be dissolved at room temperature. For efficient hydration, the individual gum particles must be well dispersed in the solvent. Hydration time is reduced with increased mixing speed. As the particle size increases, xanthan becomes easier to disperse but slower to hydrate. Generally, high ionic strength (>1–2%) or high solid content slows down hydration. With high-speed mixing, hydration takes between 15

Table 1.9 Characteristics of xanthan gum.

	Xanthan gum
E-No.	E 415
Origin	Bacterial polysaccharide from fermentation (*Xanthomonas campestris*)
Chemical composition	• Glucose • mannose • glucuronic acid
Nutritional value (in 100 g) – metabolism	210 kJ (50 kcal); slight resorption
Fibre content	Approx. 100%
Toxicology	No ADI value defined
Solubility at low temperature (H_2O)	High – 100%
Appearance of an aqueous solution	Opaque
Viscosity of solution in water	Very high, low salt contents (<0.5%) increase viscosity and stability
Impact of heat on viscosity in water (pH 7)	Viscosity decrease (but 100% reversible below 100 °C (212 °F))
Viscosity development in water at pH 7 ($T = 0$–100 °C)	Slight viscosity decrease + conformational transition
Shear stability	High – pseudoplastic with flow limit
Thickening effect	High
pH stability	High ($2 > pH > 10$)
Decomposition	Extreme acid- and enzyme-stable
Film formation	High
Emulsion stabilization	High
Gelation	No – only in combination with LBG
Gel strength and gel stability	Gel of xanthan and LBG (50 : 50 or 60 : 40) at minimum 0.3% at low salt content and neutral pH: high gel strength, gels are highly heat-stable
Gel transparency	Low
Tendency for gel synaeresis	Low (syneresis-free)
Impact of electrolytes (cations +, 2+, 3+)	No
Reaction with Ca^{2+} ions	No
Protein activity	No – precipitation possible in milk
Crystallization control	High
Synergistic effects with other hydrocolloids	+ LBG or Cassia: viscosity increase + gel formation; + Guar or tara gum: viscosity increase; + konjac: gel formation
Other synergistic effects	Addition of maximum 0.5% NaCl improves stability
Negative interactions	—
Dosage level in foods	Low, typical 0.05–0.5%

and 30 min and with a low-speed mixer it takes up to 1 h. In solution, the side chains of xanthan wrap around the cellulose-like backbone, thereby protecting it. It is thought that this is responsible for the excellent stability of xanthan gum under adverse conditions. Its solutions undergo a conformational transition during heating, which is believed to be associated with the change from a rigid ordered state at low temperature to a more flexible, disordered state at high temperatures. The temperature of conformational transition depends on ionic strength and composition of the xanthan gum molecule, especially its acid group content. Typically, for low-level salt food applications, it occurs above 90 °C (194 °F). The presence of low salt amounts helps to maintain the rigid ordered conformation of xanthan gum, which in turn causes a relative insensitivity of the viscosity to additional salt and elevated temperature. Pure solutions exhibit Newtonian flow behaviour at very low shear rates, followed by a pseudoplastic region as shear rate increases and, finally, an upper Newtonian viscosity at very high shear rates. Xanthan solutions have the visco-elastic properties of a weak gel, giving effective suspending characteristics in liquid foods such as dressings, sauces, or cakes before baking. The gum has the ability to develop extremely high viscosities even at low concentrations. Xanthan solutions exhibit exceptional stability during heating, even in the presence of salts and/or acids. As temperature increases, solution viscosity decreases but recovers almost completely upon cooling. Sterilization temperatures reduce cold viscosity by 10–20%. Solutions are independent of pH over a wide range (pH 3–10). Xanthan is compatible with most organic acids, and it is more stable than other thickeners. It can be hydrated directly in an acidic solution, but better results are achieved by preparing the gum solution first and then adding the acid. As salts reduce hydration speed, it is recommended to hydrate xanthan in water before salt addition. Once hydrated, xanthan tolerates up to 20–30% salt without viscosity change. Generally, the gum is not soluble in organic solvents, although it will hydrate directly in glycerol at 65 °C (149 °F). After hydration, a xanthan solution tolerates up to 50% ethanol or isopropanol without precipitation. It is compatible with all other food hydrocolloids and it is very resistant to enzymes (e.g. amylases, proteases, pectinases, and cellulases). Xanthan gum has strong synergies with galactomannans such as locust bean gum (LBG), guar gum, tara gum, cassia gum, and glucomannans such as konjac gum. In solution the galactose-free (smooth) regions of the mannose backbone form associations with the ordered xanthan helices, which result in a synergistic viscosity increase in the case of guar or gelation in the case of LBG. Konjac forms strong elastic gels after heating and cooling in mixtures with xanthan gum. Cassia gum exhibits similar behaviour to LBG and tara gum has synergy intermediate to that of guar and LBG [2].

Applications

The largest application area for xanthan is dressings and sauces. In cakes, it prevents sedimentation of fruit or chocolate pieces before and during baking. It increases volume, retards staling, and prolongs freshness. Xanthan is added to dairy desserts to support gel formers and reduce synaeresis. Instant dry mix

products such as beverages, soups, desserts, and low-calorie products achieve consistent particle distribution and body by xanthan.

Toxicology and Regulatory Affairs
Xanthan has had US FDA approval since 1969. In Europe, it has been approved since 1974 as food additive E 415 with a non-specified acceptable daily intake (ADI). All animal studies, biochemical, and toxicological examinations support its harmlessness. Xanthan is only slightly digested in the human intestinal tract ($0.5\,kcal\,g^{-1}$).

1.5.2 Others

Gellan

Raw Material Gellan gum is an extracellular polysaccharide produced through fermentation by the microorganism *Sphingomonas elodea* (previously identified as *Pseudomonas elodea*, but later reclassified). All the different forms of gellan gum are made from the same basic fermentation process. Large, sterile fermentation vessels are used to allow the bacteria to convert simple sugars like D-glucose and other nutrients into this polysaccharide. Once the cells have been killed and separated from the fermentation broth, the solution is further treated to produce four different types of gellan gum:

1) high-acyl unclarified gellan gum is made by precipitation with organic solvents like alcohols;
2) high-acyl clarified gum is obtained after clarification and subsequent precipitation;
3) low-acyl unclarified gum is not manufactured commercially at present;
4) low-acyl clarified gum, a de-esterified product, is made by clarification, subsequent removal of acyl groups by treatment with alkali (deacetylation at 80 °C (176 °F) at pH ~10 for 10 min), and final precipitation [3].

Chemical Composition Gellan is a linear, anionic heteropolysaccharide with a straight chain consisting of the building blocks D-glucose, L-rhamnose, and D-glucuronic acid in a molecular ratio of 1.5 : 1 : 1. The chain is made of a tetrasaccharide chemical repeat unit in which β-(1 → 4)-linked glucose, glucuronic acid, glucose, and rhamnose in α-(1 → 3) linkage are bonded together. The native product is partially esterified: the (1 → 3)-linked glucose residue contains a C2 linked L-glycerate and about 50% C6-linked acetate substituents. In its native or high-acyl form, two acyl substituents – acetate and glycerate – are present. Both substituents are located on the same glucose residue and, on average, there is one glycerate per repeat and one acetate per every two repeating unit. In low-acyl gellan gum, the acyl groups are absent. According to X-ray diffraction

studies, the molecule is supposed to adopt a double or threefold helical structure after heating and cooling [1–3].

Solubility, Viscosity, Gelation, and Properties The presence or absence of acyl groups on the gellan gum backbone has a profound effect on its physical, chemical, and functional properties. Therefore, both types, low-acyl and high-acyl, are discussed separately. In general, gellan gum is dispersible in cold water and fully soluble in hot water. The hydration temperature of low-acyl gellan gum is sensitive to the ionic environment and is particularly sensitive to divalent cations. The gum itself contains divalent cations and will only hydrate in cold, deionized water. Hydration is further inhibited by the divalent ions present in most water supplies. This effect makes low-acyl gellan gum easy to disperse in cold water without forming lumps. Subsequently, it can be hydrated by adding sequestrants or chelators, such as citrates and phosphates, to control the divalent ions, heat or a combination of both. Hence, its hydration temperature can be controlled effectively. Without sequestrants, low-acyl gellan gum requires a temperature above 75 °C (167 °F) to fully hydrate in soft water. However, it can be hydrated in cold, soft water using 0.12% sodium citrate. The pH value of solution also affects the hydration characteristics of low-acyl gum. At pH values above the pK_a of gellan gum (about pH 3.6), the gum is in a form that allows easy dissolution. If the solution pH is below 3.6, the gum will exist in a predominantly acid form that is not completely soluble. When formulating acidic products, the acid should be added after gum hydration. Dissolved sugars have an effect on gum hydration. Hydration is possible with up to 25% dissolved sugar. At higher sugar levels, the gum must be heated to be fully solubilized. Another option is to hydrate the gum in a low-sugar environment first and add the remaining sugar solids later. High-acyl gellan gum swells in deionized water, creating a consistency like a swollen starch paste. Low levels of sodium ions inhibit this swelling behaviour. The addition of sodium salts is a useful strategy to improve gum dispersion and minimize viscosity during processing. Heat is required to fully hydrate high-acyl gellan gum. It hydrates at 70–80 °C (158–176 °F), even with high ion concentrations. In contrast to low-acyl gum, the calcium effect on high-acyl gum is small and sequestrants do not facilitate hydration. Both gum types can be dispersed directly in milk and will hydrate during normal heat processing. In acidic systems, the pH must be above 4 for good hydration. Gels can be formed over a broad range of conditions. Critical parameters are pH value, temperature, sugar solids, and cation content. Gels occur at low concentrations of 0.05–0.3% and upon cooling to 30–45 °C (86–113 °F). High-acyl gellan gum forms soft elastic gels whose strengths increase in the presence of mono- or divalent cations. The gels of low-acyl gum are very firm and brittle and similar to agar gels. Sugar has a plasticizing effect on the gels, which are thermoreversible, stable at pH 3.5–8, and not attacked by enzymes. When the gellan gum concentration is high enough, the network structure becomes a demoldable gel. At lower

concentrations, the gum molecules still associate and form a long-range network; the system remains very fluid and forms a so-called fluid gel. Fluid gels exhibit a highly pseudoplastic flow property – the viscosity decreases with increasing shear. While low in viscosity, however, these gels have a high elastic modulus, which imparts suspension properties to the system. In fact, fluid gels including gellan gum have a yield stress that keeps particles in suspension.

Blends of high-acyl and low-acyl gellan gum are commonly used to produce a 'gel within a gel' and create flexibility in formulation development. Gellan is also mixed with other gelling and non-gelling hydrocolloids to modify rheology, stability, heat performance, or setting temperatures. Xanthan or CMC are added to low-acyl gellan gum to produce softer gels with a smooth texture. Low-acyl gum is used to increase the firmness of soft, elastic gels such as ι-carrageenan, gelatine, or combinations of LBG and xanthan gum. Gellan alters the setting and melting properties of other gelling agents. For example, gellan gum can be used to improve the heat stability of gelatine gels and to raise the set temperature of gelatine-based confections and dessert gels. Additionally, gummy candies can be made gelatine-free by using a mixture of carrageenan and gellan gum. Gellan strongly reduces the setting time of starch confectionary and increases the heat stability of candies, preventing them from sticking together when exposed to warm environment [3].

Application Gellan gum is used as thickener, binder, film-former, and stabilizer in a wide range of food applications. It stabilizes water-based gels such as desserts and drinking jellies. A lot of Asian food products contain the gum as alternative to agar. It is used in bakery formulations, where it does not increase the batter viscosity when cold, but hydrates during baking. It improves bake-stability of fillings with low to high soluble solids content. Gellan gum replaces gelatine in cultured dairy products such as yogurt and sour cream in vegan, Kosher or Halal nutrition. It is typically added in low concentrations (maximum 0.1%) to raw milk prior to homogenization. In beverages, gellan gum reduces cloud and pulp settling. It is suitable in systems with low milk amounts, low-quality milk protein, or heat-damaged proteins such as those found in spray-dried milk powders where carrageenan comes to its functional limit. Gellan gum gives a short texture to gelled confectionary, improves gelatine gummy candies, reduces stickiness, and shortens production time of demoldable products. Other applications are low-calorie (sugar-free) jams in which pectin is not functional, fruit preparations for yogurt, sauces, no-fat salad dressings with herbs, and films and adhesion systems [3].

Toxicology and Regulatory Affairs Gellan gum was first used and approved in 1988 in Japan, where microbial polysaccharides are considered as naturals materials. Gellan gum is now approved for use in foods, cosmetics, pharmaceuticals, and non-food products in USA, Canada, Australia, Europe, and many other countries of Latin America, South America, and Asia. The FDA has approved it

for food in the USA. There is no ADI specified. In Europe it is classified as food additive E 418 [3].

Pullulan

Raw Material and Manufacturing The manufacturing process of pullulan was developed in Japan in 1976. Pullulan is an extracellular glucan produced from starch syrup and sugar as substrate through fermentation by the fungus *Aureobasidium pullulans*, commonly called 'Black yeast'. With help of nitrogen sources and different salts, the cultivation is carried out at 30 °C (86 °F) under agitation. After 100 h, the yield is greater than 70%. To purify pullulan, the microbial cells are first removed by filtration. After decolouration with activated carbon, the filtrate is subjected to an ion-exchange process to remove the contaminating salts and proteins and to obtain a purified solution. After concentration, the solution is drum dried and pulverized to produce a fine powder [2].

Various bacteria such as *Klebsiella* species possess enzymes, the so-called pullulanases, with which they cleave pullulan and can make it available as a carbon source.

Chemical Composition Pullulan is a linear polysaccharide, a homoglucan, consisting of maltotriose building blocks. Three of the glucose units of maltotriose are linked through α-(1 → 4) glycosidic bonds while the subsequent maltotriose units are linked by α-(1 → 6) bonds. The molecular weight of the polymers is between 10 and 400 kDa.

Solubility and Viscosity Pullulan easily dissolves in cold or hot water to form a stable, viscous solution that does not gel. It is insoluble in organic solvents, with the exception of dimethylformamide and dimethyl sulfoxide. Pullulan can be modified with ethers or esters, so that, depending on the degree of substitution, it may be insoluble in water and soluble in other organic solvents such as acetone or ethanol. Pullulan solutions have a relatively low viscosity, like gum Arabic, when compared with other hydrocolloids. The solutions are Newtonian fluids with a surface tension similar to that of water (74 dyne cm^{-2}). Viscosity is essentially unaffected by pH over a wide range from pH 2 to 11 and is stable in the presence of most metal ions. With some ions, for example borate, complex formation with hydroxyl groups is observed, which leads to a strong increase of viscosity. However, even under such conditions, pullulan does not gel [2].

Properties Pullulan is a tasteless and odourless white powder. Its solutions are stable over a wide range of pH and it is relatively stable to heat. A significant feature of pullulan is its high stability to sodium chloride. Heating pullulan in 30% sodium chloride solution at 100 °C (212 °F) for 6 h produces no noticeable change in viscosity.

It is highly adhesive when dissolved in water and it has remarkable binding properties – it shows superior adhesiveness on wood compared to cornstarch

and modified cellulose. Pullulan readily forms films that are edible, transparent, oil-impermeable, anti-static, readily soluble in water, and have low oxygen permeability. The powder is directly compressible with heat and pressure in the presence of moisture. Pullulan is a biodegradable polymer. It is easily metabolized by many microorganisms found in nature to give carbon dioxide and water. But it is largely undegraded by human digestive enzymes and can be used as low-calorie food additive. Pullulan is a soluble dietary fibre with prebiotic function [2].

It can replace gelatine in coatings.

Application Pullulan is used as binder, thickener, glazing, and coating agent in food (30 vol.%). Other applications are films (30%), capsules (30%), and cosmetics and drugs (10%). Edible packaging films of pullulan are common in Japan. Pullulan is used in the coating of food supplement products. Fresh breeze strips are made with pullulan. Instant beverages, creams, icings, frostings, soy sauces, other sauces, desserts, confectionary, and processed meat products are made with the addition of pullulan (0.2–3%).

Toxicology and Regulatory Affairs In the USA, the FDA approved the GRAS (generally recognized as safe) notification for pullulan in 2002. Pullulan was recently approved in the EU as food additive E 1204 for use in capsules, tablets, and films under directive 2006/52/EC. It is also permitted in several Asian countries, in Russia, and in some South American countries. No ADI has been specified [2].

Dextran

Raw Material Dextran is produced in an extracellular process by fermentation of the disaccharide sucrose by enzymes of bacteria of the genus *Leuconostoc* or *Streptococcus*. Sucrose is the carbon source; hydrolysed yeast is the nitrogen source. The pH value is about 6.5–7. After fermentation, the culture medium is cleaned of microorganisms. The solubilized dextrans are precipitated by addition of organic solvents such as methanol, ethanol, 2-propanol, or acetone. By re-precipitation, entrained contaminants are removed. The resulting product is a white powder.

In nature, dextran serves as reserve materials for yeasts and bacteria.

Chemical Composition Dextrans are high molecular weight, highly branched, neutral biopolysaccharides. Since the polymers are composed only of glucose units, they belong to the homoglycans. Some 95% of the glucose monomers are located in the main chain, an α-(1 → 6) glucan. The glycosidic bonds to the side chains occur as α-(1 → 4) or α-(1 → 3), rarely as α-(1 → 2) linkages. Natural dextrans have molecular masses of 10–50 000 kDa.

Solubility and Viscosity Dextrans are readily soluble in water or glycerine at room temperature. Sterile aqueous solutions are very stable at pH 4–7 at room

temperature. Solubility and viscosity depend on the molecular mass and on the structure of the dextran. Highly viscous, slimy liquids can be formed.

Application The colloid osmotic pressure of a dextran solution (6% of a molecular weight of 75 kDa) corresponds to that of human blood and, therefore, dextrans are used in medicine as a substitute for blood plasma. Low molecular weight dextrans act as platelet aggregation inhibitors. Other uses are as a stabilizer in freeze-drying processes, in blood purification, and for X-ray contrast liquids. Dextrans act as carriers for gel chromatography, as molecular sieves in chemical analysis, as tablet binder, and as protective colloid for cells to prevent freezing damage. The tendency to form films makes dextrans suitable for protective coatings. Examples are improved solubility and flavour fixing for coffee and tea powders.

Toxicology Dextrans are decomposed in the human digestive tract and transferred into energy. As blood plasma expander, dextrans are excreted quickly by the kidneys. Highly branched substances can cause allergies in humans. There is no defined ADI value [1].

Curdlan

Raw Material The polysaccharide curdlan is produced in an extracellular procedure by the non-pathogenic bacteria *Agrobacterium biobar* and mutants of *Alcaligenes faecalis* var. *myxogenes*, a group of microorganisms occurring in the soil. The product is manufactured by conventional fermentation processes. It is an odourless white powder.

Chemical Composition Curdlan is a linear β-(1 → 3)-glucan (99%), a high-molecular-weight polymer of glucose with the general formula $(C_6H_{10}O_5)_n$. It contains hardly any branches. It can be partially esterified with succinic acid and occur as succino-glucan. The amount of esterified polysaccharide and degree of esterification depend on the bacteria producing it. Curdlan manufactured technically for industrial use contains only very small amounts of succinic acid. The average molecular weight is between 40 000 and 70 000 Da.

Solubility and Viscosity Curdlan is insoluble in water up to 54 °C (129 °F). Upon heating its aqueous suspensions above this temperature, it starts to swell and forms strong elastic gels. The gel strength is between that of agar and gelatine. Curdlan is soluble in aqueous alkaline solutions.

Properties Curdlan forms irreversible gels in water during heating. The strength of the gels increases with increasing temperature. It reaches a plateau at 80 °C (176 °F) and starts increasing again at 100 °C (212 °F). The gels exhibit synaeresis that strongly depends on the temperature of storage. Curdlan forms water-insoluble films with strength between those of cellulose and amylose. The films are edible, biodegradable, and impermeable to oxygen [1].

Application and Regulatory Affairs Curdlan has numerous applications as a gelling agent in the food, construction, and pharmaceutical industries. It is suitable to replace gelatine and agar in production of jellies, desserts, and confectionary. Curdlan can be used as thickener and binder in dietetic foods (e.g. in salad dressings, desserts, pasta). For long-life products, it can deliver edible coatings.

It has been approved as a food additive by the US FDA. In Japan, there is food approval, too.

Scleroglucan

Raw Material and Manufacturing Scleroglucan is the extracellular secretion of the filamentous fungus *Sclerotium*, *inter alia* the species *Sclerotium rolfsii* and *Sclerotium glucanicum*. The polysaccharide is produced by aerobic submerse fermentation in conventional fermentation tanks with controlled aeration. D-Glucose serves as carbon source and corn steep liquor or nitrate as nitrogen source. After fermentation, the fungi spawn is removed by filtration. The polysaccharide is precipitated with an organic solvent, filtrated or centrifuged, dried, and milled [1].

Chemical Composition Scleroglucan is a non-ionic neutral homoglucan consisting of D-glucose as building block. The β-(1 → 3)-glucan has one β-(1 → 6)-glucose residue as side chain every three main residues. Its molecular weight is very high (2 MDa).

Solubility and Viscosity Scleroglucan is easily soluble in cold and in hot water. It produces aqueous solutions with a very high viscosity. Owing to its non-ionic nature, acids and alkalis do not affect scleroglucan over a wide pH range (2.5–12). Mono-, di-, and trivalent cations have no impact on solution viscosity. Unlike most natural and synthetic gums, high temperature has little effect on the viscosity of a scleroglucan solution. Below 10 °C (50 °F), the solutions form a soft gel that can be eliminated by shaking or heating. Solutions of scleroglucan may be sterilized by heating them at 121 °C (250 °F) for 20 h without affecting their viscosity.

Application Besides the thermal stability, solutions of scleroglucan exhibit pseudoplastic behaviour with a high yield value, resulting in solutions of high-suspending power with good pouring properties. Because of its high yield value, it is extremely effective in holding particles in suspension, in static as well as in dynamic conditions, without any risk of sedimentation. Scleroglucan has a good emulsifying capability and acts as foam stabilizer. It is compatible, without synergism, with most other thickening hydrocolloids. It is also compatible with most widely used surfactants such as sulfates, sulfonates, and quaternary ammonium salts. Scleroglucan remains soluble in mixtures containing up to 50% of polyols and glycols.

Its remarkable rheological properties and stability over a wide range of pH values, salinities, and temperatures make scleroglucan suitable for several applications.

In Europe it is mainly used in cosmetic products for skin care and sun-care, in shower gels, body washes, shampoos, conditioners, shaving foam, make-up, mascara, and eyeliners.

1.6 Overview Tables for the Most Important Cellulose Derivatives

Tables 1.10–1.14 give an overview of characteristics and selected properties of the most important cellulose derivatives (MCC, MC, HPMC, EC, HPC, and CMC). The idea is to present the main features at a glance to simplify developmental work and check whether the substance is generally suitable for a specific application. The details for each characteristic can be studied in the respective chapter.

Table 1.10 Characteristics of powdered and microcrystalline cellulose (MCC).

	Powdered cellulose and colloidal MCC
E-No.	E 460 (i), E 460 (ii)
Origin	Wood pulp or cotton linters
Chemical composition	Linear molecule of ß-D-glucose with an increased amount of crystalline sections; colloidal MCC consists additionally of cellulose gum (CMC), alginates, guar or xanthan gum
Nutritional value (in 100 g) – metabolism	Powdered cellulose: 0 kJ (0 kcal), no resorption; MCC: depends on added hydrocolloid
Fibre content	Cellulose is 100% soluble dietary fibre
Toxicology	No health concerns, no ADI value defined, but laxative effects at 12–15 g day^{-1}
Solubility at low temperature (H_2O)	Low, only swelling (0.24% water-soluble components in powdered MCC)
Appearance of an aqueous solution	Opaque
Viscosity of solution in water	Formation of a dispersion and an extreme thixotropic stable 3D-gel after application of high shear forces
Impact of heat on viscosity in water (pH 7)	Stable viscosity (no heat-thinning)
Viscosity development in water at pH 7 (T = 0–100 °C (32–212 °F))	100% Cold water dispersible; stable viscosity upon heating
Shear stability	Shear forces activate the formation of a dispersion and thixotropic 3D-gel; viscosity of the gel is reduced by shear, but recovers to almost the initial value after a rest-time
Thickening effect	High – after shear treatment
pH stability	Medium (from pH 3.8–9); there are colloidal MCC types with added protective hydrocolloids (e.g. CMC) available to prevent flocculation
Decomposition	• By enzymes (cellulases); • flocculation by cooking in acidic systems
Film formation	Low

Table 1.10 (*Continued*)

	Powdered cellulose and colloidal MCC
Emulsion stabilization	Support of emulsifiers
Gelation	After application of high shear forces
Gel strength and gel stability	Gelation after shear treatment; spreadable heat-stable gels
Gel transparency	Opaque gels
Tendency for synaeresis	Low
Impact of electrolytes (cations +, 2+, 3+)	Low
Reaction with Ca^{2+} ions	Low
Protein activity	No for powdered MCC; added protective colloids in colloidal MCC may deliver protein activity
Crystallization control	Low
Synergistic effects with other hydrocolloids	Neutral inert character; microcrystalline cellulose does not impact other hydrocolloids because it does not consume water
Other synergistic effects	No for MCC, only possible due to interactions of the co-processed hydrocolloid
Negative interactions	At acidic pH values (<4.5) and without protective colloid, MCC flocculates to larger particle aggregates
Dosage level in foods	Medium to high, 0.1–5%

Table 1.11 Characteristics of methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC).

	Methylcellulose	**Hydroxypropylmethylcellulose**
E-No.	E 461	E 464
Origin	Wood pulp or cotton linters	
Chemical composition	Linear molecule of ß-D-glucose with:	
	Uncharged hydrophobic (CH_3) substituents	Uncharged hydrophilic ($CH_2CHOHCH_3$) and hydrophobic (CH_3) substituents
Nutritional value (in 100 g) – metabolism	0 kJ (0 kcal); no resorption	
Fibre content	93.5 g per 100 g product (100% soluble fibre)	
Toxicology	No health concerns, but laxative effects at 12–15 g per day; no ADI value defined, GRAS status of MC; long-chain HPMC channels undesired substances 'out'	
Solubility at low temperature (H_2O)	High, 100%	
Appearance of an aqueous solution	Water-clear, transparent	
Viscosity of solution in water	Low to high (5–250 000 mPa s at 2%)	
Impact of heat on viscosity in water (pH 7)	1. Viscosity decrease; 2. viscosity increase; 3. gelation – flocculation possible; 4. viscous solution upon cooling	

(*continued*)

Table 1.11 (*Continued*)

	Methylcellulose	Hydroxypropylmethylcellulose
Viscosity development in water at pH 7 ($T = 0$–$100\,°C$ (32–212 °F))	Reversible viscosity change, thickening and gelation	
Shear stability	Shear-thinning with re-thickening after a rest time, pseudo-plastic flow behaviour of aqueous solutions, gels are extremely thixotropic	
Thickening effect	Low to high	
pH stability	High (from pH 2–12)	
Decomposition	By enzymes (cellulases)	
Film formation	High	
Surface activity	High, good foam generator	Very high, excellent foamer
Emulsion stabilization	Support of emulsifiers	
Gelation	Reversible gelation upon heating, melting-back upon cooling	
Gel strength and gel stability	• High gel strength; • stable, when kept hot	• Soft to semi-firm gels; • stable, when kept hot
Gel transparency	Opaque gels	
Tendency for synaeresis	Slightly	Very low
Impact of electrolytes (cations +, 2+, 3+)	Low; high concentrations could cause reversible flocculation	
Reaction with Ca^{2+} ions	Low	
Protein activity	Low/no	
Crystallization control	High	
Synergistic effects with other hydrocolloids	No real synergistic effects	
Other synergistic effects	—	
Negative interactions	Possible with some preservatives in liquid systems (e.g. beverages with benzoate)	
Dosage level in foods	Low, 0.05–0.8%	

Table 1.12 Characteristics of ethylcellulose (EC).

	Ethylcellulose – EC
E-No.	E 462
Origin	Wood pulp or cotton linters
Chemical composition	Linear molecule of ß-D-glucose with uncharged ethyl groups as substituents (CH_2CH_3)
Nutritional value (in 100 g) – metabolism	kJ (0 kcal); no resorption
Fibre content	>99% Soluble dietary fibre in dry matter
Toxicology	No ADI value defined, but laxative effects at 12–15 g day^{-1}
Solubility at low temperature (H_2O)	Depending on DS: water-solubility at DS 0.8–1.3; only organo- and oil-soluble at DS 2.2–2.8 (commercial grades)
Appearance of an aqueous solution	Commercial grades are not water-soluble
Viscosity of solution	7–100 mPa s at 5% in 80 : 20 toluene–ethanol

Table 1.12 (*Continued*)

	Ethylcellulose – EC
Impact of heat on viscosity	Reversible viscosity decrease upon heating; no gelation
Viscosity development in oil/organic solvents at pH 7 (T = 0–100 °C (32–212 °F))	Reversible viscosity change/reduction; no gelation
Shear stability	High
Thickening effect	Low to high
pH stability	Very high (from pH 1–14); can be treated with hot concentrated alkalis, concentrated salt solutions and diluted acidic solutions
Decomposition	By enzymes (cellulases); highest stability of all cellulose ethers
Melting point	152–162 °C (305–324 °F)
Film formation	High
Emulsion stabilization	High
Gelation	Controlled gelation possible by hot-melting of EC (3–5%) at $T \geq 180$ °C (356 °F) in specific vegetable oils and subsequent cooling
Gel strength and gel stability	Rigid unelastic, but stable gels
Gel transparency	Transparent to opaque
Tendency for synaeresis	Low
Impact of electrolytes (cations +, 2+, 3+)	Low
Reaction with Ca^{2+} ions	Low
Protein activity	No
Crystallization control	Depending on DS
Synergistic effects with other hydrocolloids	No real synergistic effects
Other synergistic effects	—
Negative interactions	—
Dosage level in foods	Medium (0.5–5%)

Table 1.13 Characteristics of hydroxypropylcellulose (HPC).

	Hydroxypropylcellulose – HPC
E-No.	E 463
Origin	Wood pulp or cotton linters
Chemical composition	Linear molecule of ß-D-glucose with uncharged hydrophilic ($CH_2CHOHCH_3$) substituents
Nutritional value (in 100 g) – metabolism	0 kJ (0 kcal); no resorption
Fibre content	97% Soluble dietary fibre
Toxicology	No ADI value defined, but laxative effects at 12–15 g day^{-1}
Solubility at low temperature (H_2O)	T = 0–38 °C (32–100 °F): high, 100%; T > 40–45 °C (104–113 °F): insoluble in water (precipitation of dissolved HPC)
Appearance of an aqueous solution	Water-clear, transparent

(*continued*)

Table 1.13 (*Continued*)

	Hydroxypropylcellulose – HPC
Viscosity of solution in water	Low (10% = 200 mPa s) to high (1% = 3000 mPa s)
Impact of heat on viscosity in water (pH 7)	Strong viscosity decrease until the point of flocculation/ precipitation is achieved (reversible heat-thinning)
Viscosity development in water at pH 7 (T = 0–100 °C (32–212 °F))	100% Cold water solubility, reversible viscosity decrease upon heating up to 38 °C (100 °F); flocculation, precipitation, phase separation, significant viscosity decrease; re-dissolution upon cooling below 38 °C (100 °F)
Shear stability	Pseudoplastic flow behaviour at high shear forces, solutions of low-viscosity grades are shear-stable at moderate shear treatment
Thickening effect	Low to high
pH stability	High (from pH 2–11)
Decomposition	• By enzymes (cellulases), light, oxygen; • but more stable than other cellulose ethers
Film formation	High
Surface activity	High, good foam generator
Emulsion stabilization	Support of emulsifiers
Gelation	No gel formation
Gel strength and gel stability	No gelation in pure water
Gel transparency	—
Tendency for synaeresis	No
Impact of electrolytes (cations +, 2+, 3+)	Salts and sugar reduce the flocculation temperature
Reaction with Ca^{2+} ions	Low
Protein activity	Low
Crystallization control	High
Synergistic effects with other hydrocolloids	Viscosity win with the anionic cellulose ether Na-CMC in the pH range of 4–9 and NaCl contents of <0.5%
Other synergistic effects	Sugar and salts (NaCl) reduce the flocculation temperature
Negative interactions	—
Dosage level in foods	Low for foams: 0.1–0.5%, high for films: 10%

Table 1.14 Characteristics of carboxymethylcellulose (CMC).

	Na-CMC – cellulose gum
E-No.	E 466
Origin	Wood pulp or cotton linters
Chemical composition	Linear molecule of ß-D-glucose with negatively charged carboxymethyl substituents (COO^-)
Nutritional value (in 100 g) – metabolism	0 kJ (0 kcal); no resorption
Fibre content	Minimum 82% soluble dietary fibre
Toxicology	GRAS status, no ADI value defined, but laxative effects at 12–15 g day^{-1}
Solubility at low temperature (H_2O)	High, 100%
Appearance of an aqueous solution	Water-clear, transparent

Table 1.14 (*Continued*)

	Na-CMC – cellulose gum
Viscosity of solution in water	Low to high (30–60 000 mPa s at 2%)
Impact of heat on viscosity in water (pH 7)	Constant viscosity decrease (reversible heat-thinning)
Viscosity development in water at pH 7 (T = 0–100 °C (32–212 °F))	100% cold water solubility; reversible viscosity decrease upon heating; re-thickening upon cooling
Shear stability	Shear-thinning with re-thickening after a rest time, pseudoplastic flow behaviour of aqueous solutions, low-substituted types are thixotropic
Thickening effect	Low to high
pH stability	Medium (pH 3–10)
Decomposition	• Insolubility at pH < 3; • degradation by enzymes (cellulases); • by cooking in acidic systems (heat + pH ≤ 3.5)
Film formation	High
Surface activity	Low, no foam generation
Emulsion stabilization	Support of emulsifiers
Gelation	Only with di- and trivalent ions
Gel strength and gel stability	No gelation in pure water; spreadable gels with sufficient amount of ions (2+, 3+)
Gel transparency	Opaque gels
Tendency for synaeresis	No
Impact of electrolytes (cations +, 2+, 3+)	High impact of monovalent ions on viscosity; precipitation or gelation with di- and trivalent cations
Reaction with Ca^{2+} ions	High (gelation or precipitation)
Protein activity	High, acts as protective colloid; solubilizing effect on protein around IEP; heat protection at acidic pH
Crystallization control	High
Synergistic effects with other hydrocolloids	Viscosity win with guar and non-ionic cellulose ethers; improved gel quality with starches, κ-carrageenan
Other synergistic effects	Crosslinking of CMC with positively charged molecules (chitosan, poly-L-lysine); crosslinking of CMC with low DS and high viscosity by acids (croscarmellose)
Negative interactions	Precipitation possible with di- and trivalent cations
Dosage level in foods	Low (0.05–0.5%)

1.7 Commercial Development – Global Market

The global market for all food hydrocolloids is estimated to be a volume of about 2100 MT (US$5.5 billion) for 2014. This market value is calculated on data from the manufacturers. Taking into account that several service companies and

Table 1.15 Global market data for food hydrocolloids 2002–2006.

Hydrocolloid	2002		2004		2006			
	Volume (Mio. $)	Market Share (%)	Volume (Mio. $)	Market Share (%)	Volume (1000 MT)	Market Share (%)	Price ($ kg^{-1})	Volume (Mio. $)
Gelatine	747	25	1095	30	164	9.6	5.68	932
Starches	743	25	880	24	1270	74.3	0.81	1029
Carrageenan	302	10	305	8	39	2.3	8.36	326
Pectin	301	10	323	9	35	2.0	10.23	358
Xanthan	221	7	253	7	41	2.4	5.68	233
Agar	142	5	134	4	10	0.6	18.59	186
LBG	122	4	106	3	9	0.5	17.93	161
Gum Arabic	101	3	234	6	36	2.1	5.72	206
Alginates	92	3	94	3	12	0.7	7.48	90
Guar	53	2	74	2	45	2.6	1.39	63
CMC	66	2	85	2	29	1.7	4.38	127
MC/HPMC	49	2	45	1	5	0.3	9.46	47
MCC	45	1	50	1	9	0.5	5.96	54
Others	18	1	30	1	6	0.4	6.60	40
Sum	3000	100	3708	100	1710	100	—	3850
Growth[a)]	—	—	**+23.6%**	—	—	—	—	**+3.8%**

Source: data provided from IMR (Dennis Seisun).

a) Growth is calculated on last number for the same category (e.g. '2006 volume $' versus '2004 volume $').

Table 1.16 Global market data for food hydrocolloids 2009–2014.

Hydrocolloid	2009				Forecast 2014			
	Volume (1000 MT)	Market Share (%)	Price ($ kg^{-1})	Volume (Mio. $)	Volume (1000 MT)	Market Share (%)	Price[a)] ($ kg^{-1})	Volume (Mio. $)
Gelatine	176	9.4	4.85	853	193	9.2	4.83	932
Starches	1373	73.5	0.99	1360	1531	72.8	0.99	1516
Carrageenan	44	2.4	10.98	483	52	2.5	10.83	563
Pectin	44	2.4	11.25	495	57	2.7	11.30	644
Xanthan	50	2.7	6.52	326	64	3.0	6.47	414
Agar	11	0.6	18.45	203	12	0.6	19.33	232
LBG	10	0.5	10.10	101	11	0.5	10.64	117
Gum Arabic	40	2.1	4.05	162	46	2.2	4.04	186
Alginates	14	0.7	19.50	273	16	0.8	19.56	313
Guar	51	2.7	1.65	84	58	2.8	1.66	96
CMC	32	1.7	4.91	157	36	1.7	5.00	180
MC/HPMC	7	0.4	11.00	77	9	0.4	11.56	104
MCC	11	0.6	7.64	84	13	0.6	7.92	103
Others	6	0.3	8.17	49	7	0.3	8.14	57
Sum	1867	100	—	4707	2104	—	—	5457
Growth[b)]	**+9.2%**	—	—	**+22.3%**	**+12.7%**	—	—	**+15.9%**

Source: data provided from IMR (Dennis Seisun).

a) Forecast made with constant price.

b) Growth is calculated on last number for the same category (e.g. '2014 volume $' versus '2009 volume $').

Table 1.17 Price categories for food hydrocolloids.

Price for 1 kg of hydrocolloid (US$)				
<1	**1–3**	**3–6**	**6–8**	**8–10**
Starches	Guar	• Gum arabic • CMC • gelatine • xanthan	MCC	Alginate salts
10–12	**12–15**	**15–20**	**20–30**	**>30**
• Carrageenan (SR) • MC/HPMC • locust bean gum	• Carrageenan (Ref) • HM pectin	LM pectin	Propylene glycol alginate (PGA)	Gellan gum

distribution channels are also in involved, the business is estimated to be 20–30% higher (~US$6.6–7.1 billion per year). There is still an annual growth of physical volume of 3–5%.

Starches are the major contributors to the hydrocolloid portfolio with a market share of 70–75% of physical volume and 30% of economical volume, followed by gelatine with a market share of 9–10% of physical volume and 18–25% of economical volume. These values indicate that starches and gelatine make up more than 80% of the total hydrocolloid volume and about 50% of the total business volume.

Prices are very different over the whole range of hydrocolloids. Pure gellan gum is one of the most expensive hydrocolloids at ~US$40 kg^{-1}. Native starches are at the other end of the scale (~US$0.40 kg^{-1}). Tables 1.15 and 1.16 list global market data for the 14 most-used food hydrocolloids. Price segments can be found in Table 1.17.

To give a rough indication of price per volume, the food hydrocolloids are grouped into rough prices segments. Prices are controlled by availability of raw material, demand of other (non-food) industries, processing capabilities, and logistic conditions. Changing climate conditions or new breeding measures in the case of using remnants can dramatically reduce crops. Wars or the detection of chemical contaminants may dramatically decrease the availability of raw material. Thus, food hydrocolloids are subject to more or less strong fluctuations.

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