

7.1 The concept and effects of dietary fiber

A definition of dietary fiber is:

‘... the edible parts of plants or analogous carbohydrates that are resistant to digestion and absorption in the human small intestine with complete or partial fermentation in the large intestine. Dietary fiber include polysaccharides, oligosaccharides, lignin and associated plant substances. Dietary fibers promote beneficial physiological effects including laxation, and/or blood cholesterol attenuation and/or blood glucose attenuation’

(American Association of Cereal Chemists, 2001)

Because there is a growing belief throughout the world that natural fiber foods are an integral part of a healthy lifestyle, food producers source an increasing proportion of their raw materials from nature itself. There is a growing demand from an increasingly health-conscious consumer for reduced fat and enhanced fiber foods of all types. If this can be achieved using materials that have low calorific value, further health benefits will result. Foods containing such ingredients will need to match the quality of the original product and without adverse dietary effects. This target cannot be achieved without the scientific use of thickeners, stabilizers and emulsifiers, particularly of the ‘natural type’. This calls for fibers, which can interact with water to form new textures and perform specific functions, which calls for the use of ‘hydrocolloids’. In 2003 the world market for such hydrocolloids of the fiber type was US\$ 3.5 million and is set to grow significantly to meet the health aspirations of the consumer in the next millennium. It is the task of the food scientist to provide the hydrocolloids in the most appropriate form for inclusion in the food product. This requires an understanding of their structure and the way in which they act to produce the desired function in the food.

Dietary fiber was first described as the skeletal remains of plant cell walls, which are resistant to hydrolysis by the digestive enzymes of man. Since this

excluded polysaccharide fibers in the diet, the definition was subsequently expanded to include all polysaccharides and lignin, which are not digested by the endogenous secretions of the human digestive tract. Dietary fiber thus mainly comprises non-starch polysaccharides, and indeed has been defined by Englyst and others as the 'polysaccharides which are resistant to the endogenous enzymes of man'. Industrialized countries now generally recognize the health-giving properties of increased consumption of fiber and reduced intakes of total and saturated fat. In this respect 'fiber' is used in a non-specific way, but is generally taken to mean structural components of cereals and vegetables. More recently the concept of 'soluble fiber' has emerged which assist plasma cholesterol reduction and large-bowel fermentation.

The physical and fiber properties of such soluble and insoluble fiber allow them to perform both in a physical role and also to ferment through colonic microflora to give short-chain fatty acids (SCFA), mainly acetate, propionate, and butyrate. These have a very beneficial effect on colon health through stimulating blood flow, enhancing electrolyte and fluid absorption, enhancing muscular activity and reducing cholesterol levels.

7.1.1 The physical effect

To be effective dietary fiber must be resistant to the enzymes of the human and animal gastrointestinal tract. If physically suitable it can work effectively as a result of its bulking action. In the stomach and small intestine the fiber can increase digesta mass, leading to faecal bulking, which readily explains the relief of constipation, which is one of fiber's best documented effects. It can increase stool mass and ease laxation very efficiently. This behaviour has considerable human and agricultural importance. The growth of the ruminant animal depends on the fermentable fiber content of the stockfeed.

Soluble as well as non-soluble fibers exert their actions in the upper gut through their physical properties. Those that form gels or viscous solutions can slow down the transit in the upper gut and delay glucose absorption, best explained in terms of 'viscous drag'. Thus the reduction in glycemic response by soluble fibers can be explained.

7.1.2 Fermentation product effects

Large bowel microorganisms attack the soluble fibers, in fermentation resembling that in the rumen of obligate herbivores such as sheep and cattle. The products too are similar: short-chain fatty acids (SCFA), gases (hydrogen, carbon dioxide and methane) and an increased bacterial mass. The principal SCFA are the same in humans as in ruminants, and the concentrations are similar too, particularly for omnivorous animals with a similar digestive physiology (for example, the pig). The increased bacterial cell mass, as

noted, also has a positive effect on laxation. Faeces are approximately 25% water and 75% dry matter. The major components are undigested residuals plus bacteria and bacterial cell wall debris. These form a sponge-like, water-holding matrix which conditions faecal bulk and cell debris. The ability of different fibers to increase faecal bulk depends on a complex relationship between chemical and physical properties of the fiber and the bacterial population of the colon.

The production of SCFA and their beneficial effects in humans and ruminant species has been well established for a considerable time, but the effect was not thought to be relevant to the carnivorous dog and cat. Now this too has been demonstrated.

7.1.3 Health benefits

Whether by physical bulking action or through the production of SCFA, several health advantages are now established: Increasing fiber (20–30 g per day in humans) can eliminate constipation through increased faecal bulking and water-holding. The fermentation to produce SCFA can also assist, since propionate stimulates colonic muscular activity and encourages stool expulsion.

It was thought at one time that fiber lodged in the colon could lead to inflammation and herniation. This has now been disproved, and fiber can now relieve diverticular disease conditions, probably in the same way as it relieves constipation. Applying a solution of SCFA into the colon of ulcerative colitis patients or into the defunctioned portion of surgical patients has given rise to substantial remission in colitis. It could be that the condition arises due to a defect in the fermentation process in these patients or in the products.

SCFA stimulate water and electrolyte absorption by the mucosa and enhance their transport through improving colonic blood flow. Fiber fermentation also reduces the population of pathogenic bacteria such as *Clostridia* and can prevent diarrhoea due to bacterial toxins. Epidemiological studies have shown repeatedly that populations with high levels of fiber in their diet have reduced risk of colon cancer. Protection may be through the SCFA butyrate, which inhibits the growth of tumour cells in vitro.

When applied to the companion animal, the increased production of SCFA increases gut acidity marginally, which reduces the activity of putrefaction and pathogenic bacteria and so lowers toxin, thus reducing bad odors and bad smelling faeces. The low level of toxin production reduces the load on the liver and results in better coat and skin quality. Therefore, the aging animal can look better and produce less offensive faeces.

The behavior in the intestine can influence the immune system. Thus protection is possible against colonization by opportunistic bacteria, and the improved colonization of beneficial indigenous bacteria in the gut, which gives greater resistance to infectious bacteria.

7.1.4 Prebiotics

A balanced population of intestinal microflora needs to have a sufficient supply of substrates (most importantly carbohydrate fiber) to be able to grow. Part of this carbohydrate supply is bowel mucus and the rest consists of indigestible or only partially digestible carbohydrates or compounds derived from them. After consumption, these substances end up, wholly or partly, in the large bowel. There they are broken down further by bacteria into substances that are beneficial to humans, for example lactic, propionic, butyric and acetic acids. This results in the fall in the pH of the bowel contents while at the same time gases are formed (carbon dioxide, hydrogen, and methane).

Dietary fibers are important substrates (specifically their water-soluble fraction) including difficult to digest starch fraction (amylose), pectins, indigestible oligosaccharides (e.g. inulin) and substances like lactitol, other sugar alcohols, and the food hydrocolloids. The fall in pH caused by fermentation in the large bowel in turn leads to a reduction in the formation of secondary bile acids. These acids can damage bowel cells and this can lead to an increased risk of cancer. The pH influences the composition of the intestinal microflora and a reduction in the pH in combination with the volatile fatty acids that have been formed will protect against the settlement of pathogenic bacteria.

7.1.5 Probiotics and synbiotics

Probiotics are living organisms that, after being ingested by humans or animals, exert beneficial or health-enhancing effects by improving the characteristics of the intestinal flora. They are, for instance, used in fermented dairy products. The most important are lactic acid bacteria that (by resistance to gastric acid and bile) are able to survive passage through the stomach and small intestine. Several strains of *Lactobacillus acidophilus*, *Lactobacillus casei* and certain bifidobacteria possess this characteristic. It has been found that in humans the duration of certain kinds of diarrhoea can be limited by the intake of *Lactobacillus casei* or specific bifido bacteria.

Thus the food fiber components that can exert the beneficial effects on the colon may be divided into three categories:

- nutrients (substrates) for the intestinal microflora, also called prebiotics
- living lactic acid bacteria with a beneficial effect on the intestinal microflora, the so-called probiotics
- synergistic combination of prebiotics and probiotics, also called synbiotics.

7.2 Hydrocolloid fibers

The food fibers belong to a class of chemical materials which can generally be termed 'hydrocolloids'. It is their ability to be presented to the body in

various physical and functional forms that enables them to be so effective in a variety of food products. Their properties and main characteristics will be described. Table 7.1 gives the main hydrocolloid fibers and their food applications.

The term 'hydrocolloid' describes a group of water soluble naturally-occurring polymers found abundantly in nature. They have evolved to perform many different functions, e.g. act as structural agents and energy reserves in plants and animals, to facilitate cell recognition and adhesion processes, to provide lubrication in bone joints, to act as ion exchangers and blood anticoagulants, etc. Their key function in food products is to act as a source of fiber by controlling the texture and organoleptic properties mainly by enhancing the viscosity and gel characteristics. Even at concentrations of 1 wt% or less some hydrocolloids are capable of producing highly viscous solutions or forming gels with varying textures. Their thickening ability has led to their use as suspension and emulsion stabilizers where they function by retarding particle sedimentation and droplet creaming due to bulk viscosity effects. The hydrocolloids may also adsorb onto the surface of particles or droplets and inhibit aggregation by steric or electrostatic forces. Each hydrocolloid has its own unique functional characteristics, which is a consequence of its chemical structure, molecular size, and shape.

7.2.1 Thickening characteristics

The viscosity of hydrocolloid solutions shows a marked increase at a critical polymer concentration commonly referred to as C^* . This concentration corresponds to the transition from the so-called 'dilute region', where the polymer molecules are free to move independently in solution without touching, to the 'semi-dilute region' where molecular crowding gives rise to the overlap of polymer coils and interpenetration occurs. Hydrocolloid solutions normally exhibit Newtonian behavior at concentrations well below C^* , i.e. their viscosity is not dependent on the rate of shear. However, above C^* non-Newtonian behavior is usually observed. A typical viscosity–shear rate profile for a polymer solution above C^* shows three distinct regions:

1. a low shear Newtonian plateau
2. a shear thinning region
3. a high shear Newtonian plateau.

Microstructurally in the low shear region it is envisaged that the system is able to rearrange at a rate this is greater than the imposed deformation (i.e. the polymer molecules entangle at a greater rate than they disentangle). Above a critical shear rate, however, in the shear thinning region the rate of rearrangement is less than the imposed deformation and shear thinning results. The viscosity drops to a minimum plateau value at infinite shear rate (high

Table 7.1 Source, function and main applications of hydrocolloids

Hydrocolloid	Source	Function	Application areas
	Botanical		
Carboxymethyl cellulose	Trees and cotton	Thickener	Dairy and desserts, ready-to-eat meals, bakery products, meat products, sauces and dressings. Reformed vegetables, fish cakes etc.
Methyl- and hydroxypropyl methyl-cellulose		Thickener and gelling agent	
Modified starches	Corn, potato, etc.	Thickener and gelling agent	Ready-to-eat meals, dairy and desserts, meat products, soups, bakery products, sugar confectionery
Pectin	Citrus peel and apple pomace	Gelling agent	Jams, fruit preparations, sugar confectionery
Guar gum	Seed endosperm (<i>Cyamopsis tetragonoloba</i>)	Thickener	Dairy and desserts, bakery, petfoods, ready-to-eat meals, sauces and dressings
Locust bean gum	Seed endosperm (<i>Ceratonia siliqua</i>)	Thickener	Dairy and desserts
Tara gum	Seed endosperm (<i>Cesalpinia spinosa</i>)	Thickener	As guar and locust bean gum but limited application at present
Gum arabic	Tree gum exudate (<i>Acacia senegal and seyal</i>)	Produces low viscosity solutions at gum concentrations Emulsifier	Sugar confectionery, beverages
Gum karaya	Tree gum exudate (<i>Sterculia urens</i>)	Thickener	Dressings but usage limited
Gum tragacanth	Tree gum exudate (<i>Astragalus gummifer</i>)	Thickener	Dressings and sauces, icings but usage limited.
Konjac mannan	Tuber <i>Amorphophallus konjac</i>	Thickener and gelling agent	Japanese noodles, jelly desserts

(Continued)

Table 7.1 (Continued)

Hydrocolloid	Source Botanical	Function	Application areas
	Algal		
Agar	Red seaweeds (<i>Gelidium</i> , <i>Gelidiella</i> and <i>Pterocladia</i>)	Gelling agent	Confectionery, dairy and desserts
Carrageenan <i>Kappa type</i>	<i>Euchema cottonii</i> and <i>Chondus crispus</i>	Gelling agent	Dairy and desserts, meat products, petfoods, sugar confectionery
<i>Iota type</i>	<i>E. spinosum</i>	Gelling agent	
<i>Lamba type</i>	<i>Chondus crispus</i>	Thickener	
Alginate	Brown seaweeds (<i>Laminaria hyperborea</i> , <i>macrocystis pyrifera</i>)	Gelling agent	Dairy and desserts, bakery products, petfoods, sugar confectionery
Propylene glycol alginate		Emulsion and foam stabiliser	Salad dressings, beer
	Microbial		
Xanthan gum	(<i>Xanthomonas campestris</i>)	Thickener	Dairy and desserts, ready-to-eat meals, sauces and dressings, petfoods
Gellan gum	(<i>Sphingomonas elodea</i>)	Gelling agent	Sugar confectionery, dessert jellies, fruit preparations
	Animal		
Gelatin	Cattle, pigs, fish	Gelling agent	Sugar confectionery, meat products, dairy and desserts
Milk proteins	Cattle	Gelling agent	Bakery products, dairy and desserts, confectionery

shear region). A number of empirical mathematical models have been developed to describe the flow characteristics.

The most widely used model to describe the whole shear rate range is probably the Cross equation;

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta}{1 + (\tau\gamma)^m}$$

where, η is the viscosity at infinite shear rate, η_{∞} is the infinite shear viscosity, η_0 is the zero shear viscosity, τ is a shear dependent constant denoting the onset of shear thinning, $\dot{\gamma}$ is shear rate and m is an exponent quantifying the degree of shear thinning. m has a value of 0 for a Newtonian solution and increases to 1 with increased shear thinning.

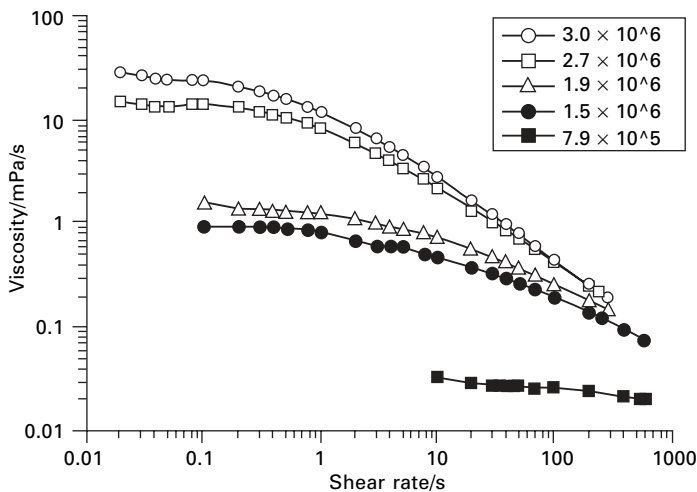
The viscosity of hydrocolloid solutions is influenced significantly by the polymer hydrodynamic volume, which increases with radius of gyration (R_g). R_g increases with molecular mass, chain rigidity, and electrostatic charge density and is greater for linear compared to branched hydrocolloids. The main hydrocolloid thickeners used are listed in Table 7.2. The viscosity shear rate profiles for 1% solutions of some of these hydrocolloids are presented in Fig. 7.1. The most striking feature is the profile for xanthan gum. This hydrocolloid has a very high low shear viscosity, and hence it is good at suspending particles and oil droplets. In addition, however, it is also extremely shear thinning and, therefore, it readily flows on simple shaking. These characteristics have led to its widespread use in many food applications, notably, mayonnaise, dressings, and sauces.

7.2.2 Gelling characteristics

A number of hydrocolloids are able to form gels by physical association of their polymer chains through, for example, hydrogen bonding, hydrophobic association, cation mediated cross-linking, etc. and differ from synthetic polymer gels which normally consist of covalently cross-linked polymer chains. Certain helix forming hydrocolloids, for example, agarose, carrageenan,

Table 7.2 Main hydrocolloid thickeners

Hydrocolloid	Characteristics
Modified starches	Viscous solutions are formed depending on the type of modification.
Xanthan gum	Has an apparent yield stress and hence can prevent sedimentation and creaming, but solutions are highly shear thinning. Viscosity is not influenced by temperature, addition of salts or to pH changes.
Carboxymethyl cellulose	Viscous solutions are formed but the viscosity decreases on addition of salts and at low pH.
Methylcellulose and hydroxymethyl cellulose	Form viscous solutions which gel on heating.
Galactomannans (guar and locust bean gum)	Form highly viscous solutions which are not influenced by addition of salts or changes in pH.



7.1 Viscosity-shear rate profiles for 1% solutions of guar gum of varying molecular mass.

gellan gum and gelatin, form gels on cooling. These hydrocolloids adopt a disordered conformation at high temperatures but on cooling they undergo a conformational change and ordered helices are formed. The helices then aggregate to form a gel. The process is thermally reversible and hence the gels melt on heating. The melting temperature is often higher than the gelation temperature since melting only occurs after disaggregation of the helices. It is interesting to note here that mixing solutions of xanthan gum and locust bean gum (two non-gelling polysaccharides) results in the formation of very strong gels on cooling. This has been attributed to molecular association between ordered xanthan helices and 'bare' mannan regions along the locust bean gum chain. Non-thermoreversible gels can be formed by cross-linking chains with divalent cations. Alginate and LM pectin are typical examples. Some hydrocolloids, notably methyl- and hydroxypropylmethyl-cellulose form thermoreversible gels on heating. Chain association is believed to be due to hydrophobic bonding.

Gel formation only occurs above a critical minimum concentration, which is specific for each hydrocolloid. This concentration is not the same as the critical overlap concentration, C^* , noted above. Agarose, for example, will form gels at concentrations as low as 0.2% while for acid-thinned starch a concentration of ~15% is required before gels are formed. The properties of individual hydrocolloid gels vary considerably in strength and elasticity due to differences in the number and nature of the junction zones and the degree of chain aggregation. The main hydrocolloid gelling agents and their characteristics are summarized in [Table 7.3](#).

Table 7.3 Main hydrocolloid gelling agents

Hydrocolloid	Characteristics
Modified starch	Amylose containing starches will form thermally irreversible opaque gels.
Gelatin	Forms thermoreversible gels on cooling. Gels are elastic and melt at body temperature.
Agar	Forms thermoreversible turbid, brittle gels on cooling (~40°C). Gels melt only at high temperatures (~85°C).
Kappa carrageenan	Forms thermoreversible slightly turbid gels on cooling to 40–60°C, which is promoted by the presence of potassium ions. Melting occurs at 5–20°C above gelation temperature. Gels tend to be brittle and hence it is often used in combination with locust bean gum, which gives increased elasticity, improves clarity and reduces syneresis.
Iota carrageenan	Forms thermoreversible elastic gels on cooling to 40–60°C. Melting occurs 5–20°C above the gelation temperature.
Low methoxy pectin	Forms thermoreversible gels on cooling in the presence of calcium ions and sequesterant (e.g. citrate) at pH 3–4.5.
High methoxyl pectin	Gels are formed at high soluble solids content at pH < 3.5. Gels are not thermoreversible.
Gellan gum	Forms highly transparent gels on cooling in the presence of electrolyte. Low acyl gels are brittle and are often not thermally reversible. High acyl gels are elastic and thermoreversible. They set and melt at ~70–80°C.
Methyl and hydroxypropylmethyl cellulose	Form thermoreversible gels on heating.
Alginate	Gels are formed on addition of polyvalent ions (usually calcium). Homogeneous gels are formed by generating the calcium ions in situ. Gels do not melt on heating.
Xanthan gum	Forms highly elastic thermoreversible gels with locust bean gum and konjac mannan.
Konjac mannan	Forms non-thermoreversible elastic gels in the presence of alkali.

7.3 The main hydrocolloids

7.3.1 Gum arabic

The main tree gum exudate is gum arabic, and it is also the most important commercially. Gum arabic occurs as a sticky liquid that oozes from the stems and branches of acacia trees (notably *Acacia senegal* and *Acacia seyal*)

which grow across the Sahelian belt of Africa, principally Sudan. The gummosis process occurs when the tree is subjected to stress conditions such as heat, drought or wounding. The liquid dries in the sun to form glassy nodules, which are collected by hand Fig. 7.2.

This natural fiber remains the most versatile food additive now available because of its range of functionalities. Gum arabic is the acidic polysaccharide exudate currently derived from two acacia tree sources: *Acacia senegal* and *Acacia seyal*. The Gum arabic-yielding acacias grow in semi-arid areas and the vast majority of the product which enters international trade originates in the so-called gum belt of Sub-Saharan Africa. The belt occurs as a broad band from Mauritania, Senegal and Mali in the west, through Burkina Faso, Niger, northern parts of Nigeria, Chad to Sudan, Ethiopia and Somalia in the Horn of Africa. Modern gum arabic trade has been dominated by the Sudan. Thus production in Sudan over the years gives a good indicator of consumption world-wide. Towards the end of the 1960s, total gum arabic production in Sudan (hashab and talha) was in excess of 60 000 tons. Events, mainly drought,



7.2 Collecting gum arabic from *Acacia senegal* trees.

locusts and political instability in the 1970s and 1980s led to fluctuation in both the supply and the price, and as a consequence led to changes in demand. The severe Sahelian drought of 1973–74 resulted in a world shortage and high prices, which in turn accelerated the search for substitutes such as gelatine, maltodextrins and modified starches. A low point of approximately 20 000 tons of Sudanese exports was reached in 1975, which recovered to around 40 000 tons during 1979. A further drought in 1982–84 saw levels of exports fall to below 20 000 tons in the mid-1980s and early 1990s. Sudan now faces an embargo on its products in the United States for its alleged terrorist supporting activities. In 2004 the civil war in Darfur further disrupted supplies and led to the price increasing dramatically.

Europe is the biggest regional market for gum arabic, and imports averaged 29 300 tons per year over the seven-year period 1989–95, with peaks of 32 100 tons in 1991 and 34 000 tons in 1994. France and the United Kingdom are the biggest markets, although both re-exported large proportions of their imports, which averaged 10 000 and 7900 tons per year respectively. France shows an upward trend over the seven years while the United Kingdom trend has been downward. Germany and Italy were the next biggest markets, averaging 4200 tons and 3700 tons, respectively. Outside Europe, the United States is the largest market for gum arabic. Imports averaged 10 000 tons in 1994. Japanese imports averaged 1900 tons over the seven-year period. The applications and use of gum arabic in the fiber health food market continues to increase and in 2001 income from this hydrocolloid was US\$130 million. Detailed accurate current statistics are now readily available.

Of the other producers Nigeria is the next most important after Sudan, averaging exports of between 4000 and 7000 tons. Chad comes next, and has increased its production each year since 1990, reaching 5400 in 1995. The upward trend has continued, often due to gum originating in the Sudan finding its way out through Chad. Currently (2005) the best estimate of the overall annual usage of gum arabic is 40 000–50 000 tons.

The variability of supply over the past 20–30 years has led to dramatic fluctuations in price and in turn injected uncertainty into the user market. When supplies almost dried up in the 1970s the price increased from about US\$1500 to US\$5000 per metric ton. It is impossible to evaluate the equivalence to today's prices since inflation in commodity prices has been uneven and less than in manufactured goods. The price stabilized in 1996 to around \$5000 per ton, but then overnight the Sudanese dropped their price to \$2500 per ton which led to consternation and extreme problems for the industry's processors, who were left holding stocks at the higher price. This cyclic nature of the supply and price has led to less utilization of this wonderful gum than there would otherwise have been. Large companies are uncertain whether they should have too many of their products dependent on this uncertain supply chain.

Gum arabic is a complex polysaccharide consisting of galactopyranose (~44%), arabino-pyranose and furanose (~25%), rhamnopyranose (14%), glucuropyranosyl uronic acid (15.5%) and 4-O methyl glucuropyranosyl uronic acid (1.5%). It also contains a small amount (~2%) of protein as an integral part of the structure. Analysis of the carbohydrate structure has shown that it consists of a core of $\beta(1,3)$ -linked galactose units with extensive branching at the C6 position. The branches consist of galactose and arabinose and terminate with rhamnose and glucuronic acid. It has been shown that the gum consists of three broad molecular fractions, which differ principally in their size and protein contents. Most of the gum (~90%) contains very little protein and has a molecular mass of $\sim 2.5 \times 10^5$. A second fraction, ~10% of the total, contains ~10% protein and has a molecular mass of $1-2 \times 10^6$ and has been shown to have a 'wattle-blossom'-type structure where blocks of carbohydrate of molecular mass $\sim 2.5 \times 10^5$ are connected to a common polypeptide chain (Fig. 7.3). The third fraction, ~1% of the total, contains up to 50% protein and has a molecular mass of $\sim 2 \times 10^5$. The high degree of branching gives rise to a very compact molecular structure for all of the fractions and results in solutions of very low viscosity. The second fraction has been shown to be responsible for the gum's excellent ability to stabilize oil-in-water emulsions. A major use of gum arabic is in the confectionery industry. It is also used as an emulsifier for flavor oils for incorporation in soft drinks. Encapsulation of the flavor oil can be achieved by spray drying the emulsion to form a solid powder which can be added to dried soup and cake mixes.

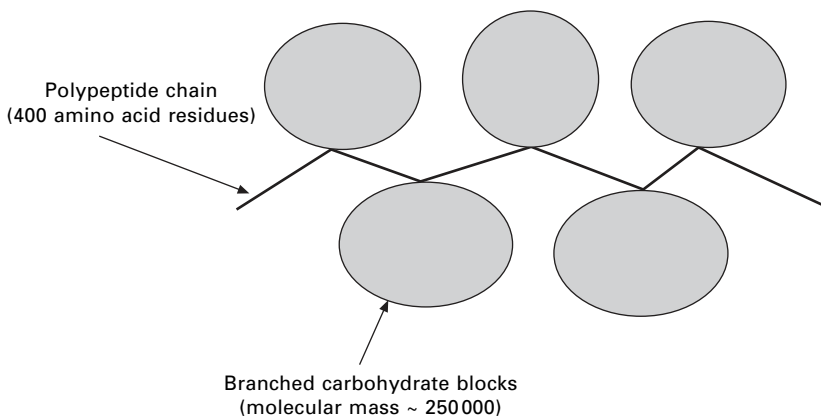
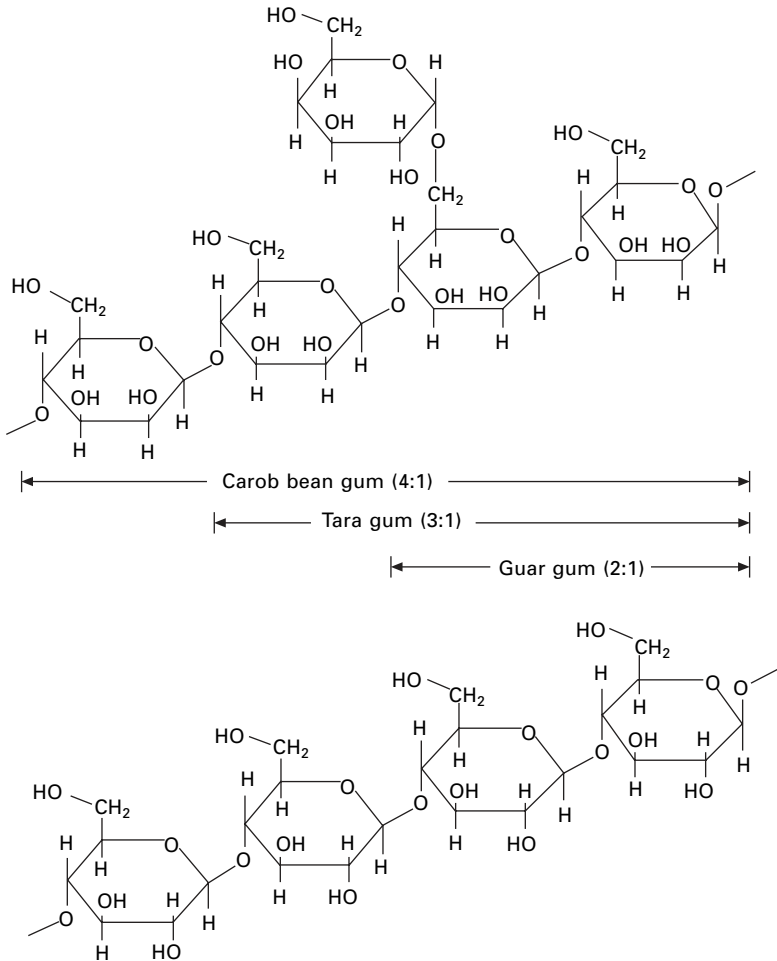


Figure 7.3 Wattle blossom-type structure of the high molecular mass fraction of *Acacia senegal* gum.

7.3.2 Galactomannan seed gums

Locust bean (or carob), tara and guar gums are storage polysaccharides obtained from the endosperms of leguminous seeds of *Ceratonia siliqua*, *Caesalpinia spinosa* and *Cyamopsis tetragonoloba*, respectively. They consist of a linear main chain of β -(1,4)-linked mannopyranosyl units with galactopyranosyl units linked (1,6) to varying degrees (and have a molecular mass of the order of 10^6) (Fig. 7.4). The mannose to galactose ratio, (M/G), is approximately 4.5:1, 3:1 and 2:1 for locust bean, tara, and guar gums, respectively. The galactose residues have been shown to be non-uniformly



7.4 Basic structural fragment of carob-, guar-, tara gum and cellulose.

distributed along the mannan chain. The presence of galactose tends to inhibit intermolecular association. Therefore, whereas guar gum is readily soluble in cold water, tara and locust bean gums have to be heated to high temperatures to achieve complete dissolution. Once dissolved all three yield highly viscous solutions. Locust bean gum will self-associate in solution and can form thermally irreversible gels on freezing. It is commonly used in combination with other polysaccharides, particularly kappa carrageenan, since it leads to the formation of stronger, more elastic gels, which have improved transparency and are less prone to undergo syneresis. Locust bean gum also forms strong thermoreversible gels with xanthan gum. For both mixtures it has been argued that the synergistic behavior is due to association of the ordered carrageenan and xanthan chains with mannose sequences along the backbone which are devoid of galactose residues. The model, therefore, explains why such behavior is not observed in mixtures containing guar gum.

Guar gum and locust bean gum are used as thickeners in a broad range of food products including dairy products, desserts, bakery products, pet foods, ready-to-eat meals, sauces, and dressings.

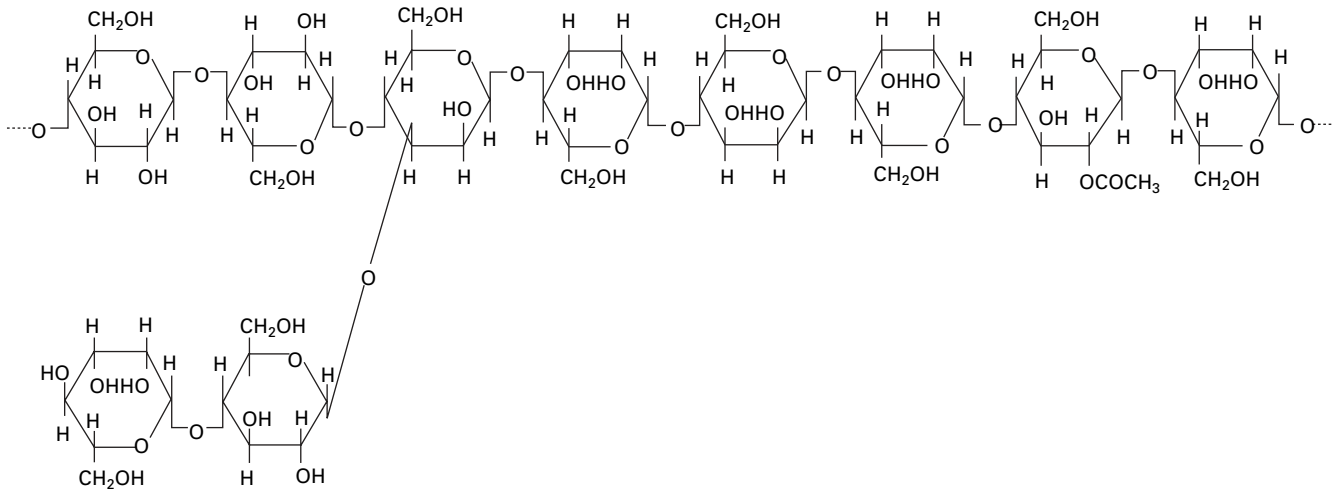
7.3.3 Konjac mannan

Konjac mannan (KM) is a glucomannan obtained from the tuber of the konjac plant notably the *Amorphophallus konjac* species which grows in Southeast Asia particularly Japan, China, and Indonesia. It is a high molecular mass ($>10^6$) polysaccharide consisting of linear chains of glucose and mannose units linked β -(1,4). Possible structures for the repeating unit are:

1. (G-G-M-M) M-M-G-M and G-G-M-G-M-M-M-M
2. (M-M-M-G-G)
3. G-G-M-M-G-M-M-M-M-G-G-M.

The main chain has branches, approximately every 10 residues, of up to 16 sugar units linked to the C3 position of the glucose and mannose. The mannose to glucose ratio is 1.6:1 and it is believed that there are no block sequences of glucose or mannose along the chain (Fig. 7.5). It has also been reported that KM has side chains and the branching position is considered to be the C3 position or C3 positions on both glucose and mannose. The degree of branching is estimated at approximately three for every 32 sugar units and elsewhere at one for every 80 sugar residues. The length of the branched chain was evaluated as 11 to 16 hexose residues.

Konjac mannan dissolves in water to form highly viscous solutions. It is acetylated (~1 acetyl group for every 19 sugar residues) and in the presence of alkali, deacetylation occurs and thermally irreversible gels are produced. Konjac mannan interacts with kappa carrageenan and xanthan gum in much



7.5 Chemical structure of konjac mannan.

the same way as locust bean gum although the gels formed are considerably stronger.

Konjac flour has been used as an important food ingredient for more than a thousand years. With the addition of a mild alkali such as calcium hydroxide, konjac flour aqueous solution (ca. 3% of concentration) changes to a strong, elastic and irreversible gel. The alkali-treated konjac gel is quite popular in traditional Japanese food and is called Kon-nyaku in Japanese. Recently, synergistic gels prepared by mixing with other hydrocolloids are major products in the food industry as new types of healthy jellies.

Clinical studies indicate that konjac mannan solution has the ability to reduce serum cholesterol and serum triglyceride. Konjac mannan also has an influence on glucose tolerance and glucose absorption. However, the alkali-treated gel food does not have such effects.

The Food Chemical Codex lists the current uses of konjac flour in the United States as gelling agent, thickener, film former, emulsifier, and stabilizer. Konjac flour is also used as a binder in meat and poultry products. Konjac flour is suitable for thickening, gelling, texturing, and water binding. It may be used to provide fat replacement properties in fat-free and low-fat meat products. Applications and functional uses of konjac mannan are listed in Table 7.4.

7.3.4 Xanthan gum

Xanthan gum, discovered in the 1950s, was the second microbial polysaccharide after dextran to be commercially exploited and is now finding extensive application in the food industry. The gum is obtained from the genus *Xanthomonas*, notably *X. campestris* by aerobic fermentation. The xanthan molecules have a $\beta(1,4)$ -linked glucopyranose backbone as in cellulose and in addition have a trisaccharide side-chain on every other glucose residue linked through the C3 position. The side-chain consists of two mannopyranosyl residues linked on either side to a glucuropyranosyl uronic acid group. The

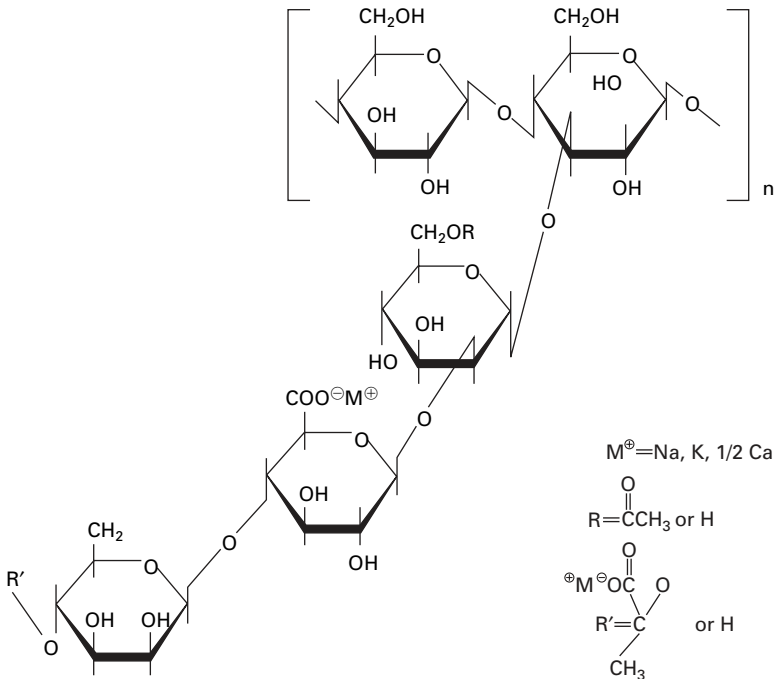
Table 7.4 Applications and functional uses of konjac mannan

Application	Function
Confectionery	viscosity, texture improver, moisture enhancer
Jelly	gel strength, texture improver
Yogurt	fruit suspension, viscosity, gelation
Pudding	thickening, mouthfeel
Pasta	water holding capacity
Beverage	fiber content, mouthfeel
Meat	bulking, fat replacer, moisture enhancer
Edible film	water soluble, water insoluble

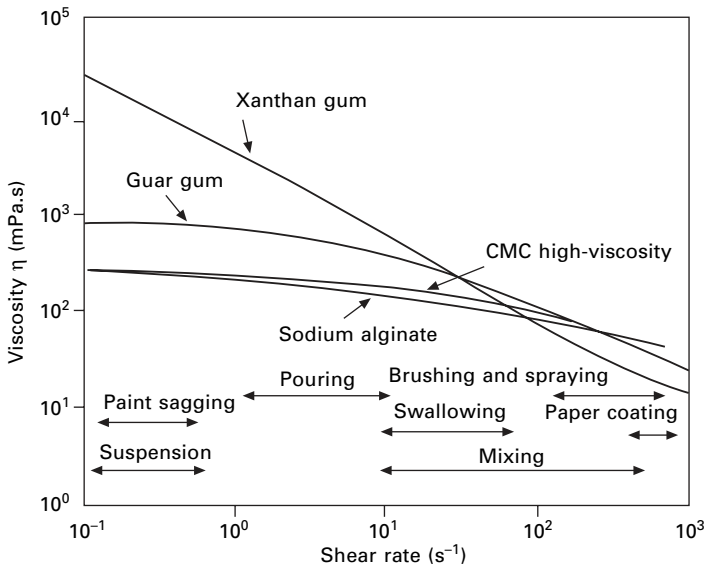
inner mannose residue connected to the backbone may be acetylated while the terminal mannose residue may be pyruvated (Fig. 7.6).

The molecular mass of the xanthan molecules is very high ($> 3 \times 10^6$) and the gum dissolves in water to yield highly viscous solutions. The xanthan molecules undergo a thermoreversible coil-helix transition in solution, which is shifted to higher temperatures by the addition of electrolyte. In the disordered coil form the side-chains are envisaged as protruding away from the backbone into solution, while in the ordered form the molecules form a stiff five-fold helical structure with the side-chains folded in and associated with the backbone. It is now generally recognized that the helix is double stranded. The stiffness of the xanthan chains gives rise to highly shear thinning rheological properties and unlike other polyelectrolytes the viscosity of xanthan solutions can actually increase rather than decrease on addition of electrolyte since the electrolyte will promote helix formation and association.

Xanthan gum is finding increasing use in a variety of applications including batter coatings, cake batters, frozen and chilled dairy products, sauces, and dressings. A comparison of the flow behavior of xanthan with other hydrocolloids is shown in Fig. 7.7. It is these excellent characteristics which make it the most versatile hydrocolloid currently used in food systems.



7.6 Primary structure of xanthan gum

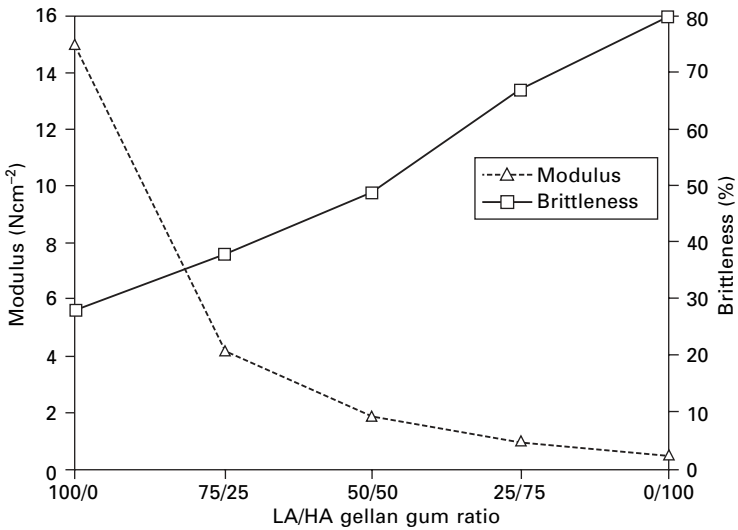


7.7 Comparison of the flow behavior of xanthan gum with other hydrocolloid solutions (0.5% concentration).

7.3.5 Gellan gum

Gellan gum has only relatively recently been commercialized. It is produced from *Sphingomonas elodia* by aerobic fermentation and consists of a linear tetrasaccharide repeat unit of β -D-(1,3)-glucopyranose- β -D(1,4)-glucuronopyranose- β -D-1,4)-glucopyranose- β (1,4)-rhamnopyranose. In the native form the β -(1,3) glucose residues contain glycerate and acetate moieties. X-ray fiber diffraction studies indicate that the gellan molecules form a three-fold double helical structure and in solution undergo a thermoreversible coil-helix transition. The transition shifts to higher temperatures in the presence of electrolyte. Once formed the helices tend to self associate leading to the formation of a transparent gel. Gels formed in the presence of monovalent ions are usually thermoreversible although the melting temperature is normally much greater than the gelation temperature, a consequence of the extensive aggregation. If gels are formed by the addition of divalent ions then they can be thermally irreversible. The native form produces soft elastic gels whereas the deacetylated material sold commercially forms hard brittle gels.

Gellan gum finds increased application at present in dessert jellies, sugar confectionery, dairy products, fruit preparations and as a suspending agent [Fig. 7.8](#) illustrates the comparison of gellan gum with other common gelling agents.

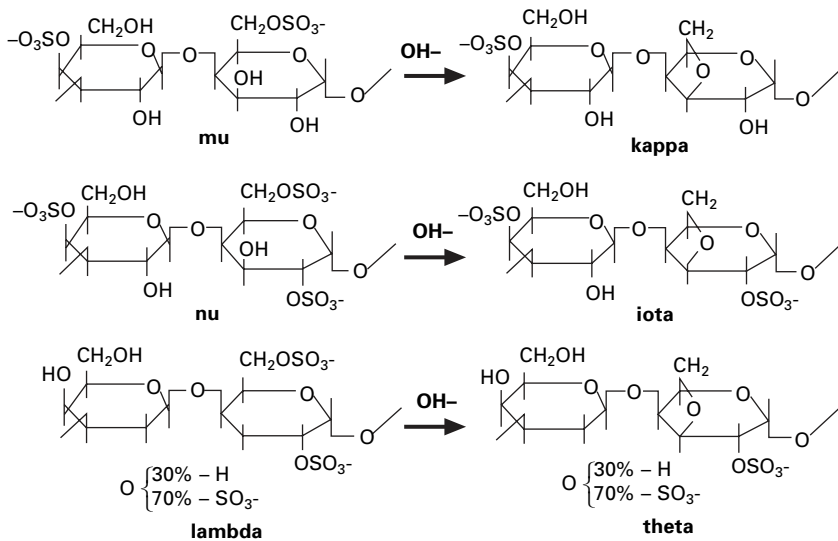


7.8 Effect of high and low acyl gellan gum blend ratio on the modulus and brittleness of gels prepared at 0.5% total gum concentration.

7.3.6 Carrageenan

The carrageenans are a family of sulphated galactans obtained from red seaweeds (*Rhodophyceae*) where they have a key structural function. The traditional method of extraction is by treatment of the seaweed with hot alkali for 10–30 hours followed by precipitation with alcohol and then drying. The three major types are kappa, iota, and lambda carrageenan. Kappa is obtained from a species of seaweed called *Euchema cottonii* and occurs together with lambda carrageenan in *Chondrus crispus*. Iota carrageenan is obtained from *Euchema spinosum*. They differ essentially in their degree of sulphation.

Carrageenan is a high molecular weight linear polysaccharide comprising repeating galactose units and 3,6-anhydrogalactose (3,6AG), both sulphated and non-sulphated joined by alternating β -(1-3) and β -(1-4) glycosidic links (Fig. 7.9). Iota carrageenan differs only in that the latter residue is sulphated at the C2 position. Lambda carrageenan is further sulphated and consists of (1,4)-linked galactopyranose 2,6 disulphate and (1,3)-linked galactopyranose which are 70% substituted at the C2 position. The carrageenans are all soluble in water but whereas lambda forms viscous solutions, kappa and iota form thermoreversible gels. The gelation mechanism is similar to that described for gellan gum above, i.e. on cooling the molecules undergo a conformational



7.9 Carrageenan structures (alkali conversion of mu > kappa, nu > iota and lambda > theta).

coil to helix transition and the helices self-associate giving rise to a three-dimensional gel structure. It is still not conclusively proven whether the helices are double or singly stranded. The temperature of gelation increases with increasing electrolyte concentration. It has been shown that potassium, rubidium, and caesium ions specifically bind to the helical structure of kappa carrageenan and hence promote helix formation and gelation at much lower concentrations than other electrolytes. As a consequence kappa carrageenan gels are much stronger in the presence of potassium chloride compared to, say, sodium chloride. This ion specificity is not observed for iota, which forms weaker more elastic gels compared to kappa. This is probably due to the fact that the increased charge on the iota carrageenan chains reduces the extent of helix self-association.

Carrageenan is used in dairy and dessert products such as puddings, milk shakes, ice cream and water dessert jellies. It is also used in meat products where it acts as a water binder.

Mention should also be made of a 'semi-refined carrageenan' from the Philippines which has now gained acceptance after a controversial start. It is now an accepted regulatory ingredient for food use under the name 'Processed Eucheuma Seaweed'.

alginate dissolves readily in water to form viscous solutions and forms thermally irreversible gels in the presence of divalent cations (notably calcium). It is the guluronic acid residues that are responsible for gel formation and their proportion and distribution along the polyuronan chain have a major influence on the properties of the gels produced. Adjacent diaxially linked guluronic acid residues form a cavity which acts as a binding site for cations which interact with the carboxyl and hydroxyl groups. Intermolecular cross-linking of sequences results in the formation of junction zones and a three-dimensional gel network. This mechanism has been described as the egg-box model. If the divalent cations are added rapidly to sodium alginate in solution unhomogeneous gels are produced. In order to produce homogeneous gels a common practice is to generate the cross-linking ions slowly in situ. Soluble salts such as calcium sulphate are used sparingly and the release of ions is controlled by the presence of sequesterants and adjustment of pH.

Alginate is used in many food products including dairy products, desserts, fruit pie fillings, structured fruit, and sugar confectionery. Propylene glycol alginate is used to stabilize foam on beer and is particularly effective at stabilizing salad dressings.

7.3.9 Gelatin

Gelatin is denatured collagen, which is a protein and major constituent of the white fibrous connective tissue occurring in the hides, skins and bones of animals. It is obtained mainly from cattle and pigs although since the outbreak of BSE in the 1990s alternative sources, notably fish, have been investigated. The collagen is extracted from the raw material by subjecting it to either acid or alkaline treatment. Acid treatment involves immersing in cold dilute mineral acid (pH 1.5–3.0) for up to 30 hours while for alkaline treatment the raw material is steeped in saturated lime water (pH 12.0). The material is then washed with water leading to the Type A (acid treatment) and Type B (alkaline treatment) gelatins. The main amino acids are glycine, proline, alanine and 4-hydroxyproline for both types. Type A gelatin contains lower amounts of glutamic and aspartic acids and hence the isoelectric point for Type A is in the range 7–9.4 while for Type B it is in the range 4.8–5.5. In solution above ~40°C the gelatin molecules are in the form of random coils but on cooling the chains tend to order and form collagen-like triple helices which aggregate to form optically clear elastic gels.

Gelatin is widely used in confectionery, meats, dairy and dessert products.

7.3.10 Cellulosics

A variety of cellulosic fiber products can be produced from wood pulp. Since these are a good source of fiber and have a variety of functionalities in

food, they seek to compete with the traditional natural hydrocolloids by offering security of supply, quality, and price. Novogel and Avicel are two examples. Both of these forms of cellulose fiber have uses in food. When properly dispersed in water systems, Avicel cellulose sets up a network with particles less than 0.2 micron in size. These particles are held together by hydrogen bonds which continue to form over a period of 24 hours, resulting in an increase in viscosity. Unlike soluble hydrocolloids the Avicel cellulose binds water to a much lesser extent. It is the physical network that affects the moisture in food systems. The applications are varied.

The gels made with Avicel cellulose readily break down with shear, but when the shear is removed the gel will reform (thixotropy). Temperature has very little effect on the functionality and viscosity of these dispersions and so they can be used during baking, processing, and microwave heating. Additionally the fiber is non-caloric and so can be used as a source of dietary fiber. Avicel cellulose can also be used to stabilize foams and emulsions. Novogel, a variant, differs from Avicel in that it capitalizes on the unique interaction between guar gum and microcrystalline cellulose. It is co-processing of cellulose gel and guar gum that imparts the special fat-like properties. These have a wide range of applications, as shown in [Table 7.5](#).

Primacel is another cellulosic product, based on fermentation of cellulose, in combination with various co-agents and can be used as a highly efficient thickener, stabilizer, and film former. It can be used as a starch extender and in addition can be used to modify texture to give a more creamy mouthfeel in low-fat food systems.

Cellulose is produced by plants and it is a major structural part of the skeletons of plants. Fine crystal cellulose or fibrillated cellulose, obtained by pulverizing cellulose through chemical and physical treatments, is widely used as a food additive.

Cellulose can also be produced by microorganisms, such as *Acetobacter*. This cellulose of bacterial origin has been eaten for many years as a dessert food called nata de coco. The addition of fermentation-derived cellulose in a very small amount will give foods good dispersion and emulsion stability, and will also give foods short mouthfeel based on a good shape retainability. These functions are largely due to the three-dimensional network structure of cellulose fibers and are stable to physical and chemical treatments; they are also resistant to heat, acids, and salts. These characteristics enable fermentation-derived cellulose to be applied to foods for a wide range of purposes such as stabilization of thickening, dispersion, suspension, and emulsion, replacement of fat, prevention of protein aggregation, etc.

7.3.11 β -Glucans

The mixed linked (1 \rightarrow 4), (1 \rightarrow 3)- β -glucans (referred to as β -glucans) are linear polysaccharides composed of cello-oligomers separated by single (1 \rightarrow 3)-

Table 7.5 Examples of the applications of fermentation-derived cellulose

Food	Effect
Cocoa drinks	Stabilizing dispersion of insoluble solid matters
Matcha drinks	Improving heat stability
Ca-strengthened drinks	Achieving good mouthfeel without raising viscosity much
Non-oil dressings	Stabilizing dispersion of insoluble solid matters Achieving clear-cut mouthfeel without raising viscosity much Achieving appropriate flowability Improving stability at low pH Achieving fatty mouthfeel
Sauce for roast meat	Stabilizing dispersion of insoluble solid matters Decrease in threading Achieving non-gluey good mouthfeel Improving stability at high salt concentration Improving stickiness
Low-fat mayonnaise	Improving creamy mouthfeel Replacing fat Achieving appropriate flowability Achieving full body
Jellies with fruit flesh	Stabilizing dispersion of insoluble solid matters Achieving heat stability Achieving good meltability in the mouth
Retorted pudding	Preventing milk protein from aggregation Achieving heat stability Achieving good meltability in the mouth
Lacto-ice	Improving creamy mouthfeel Improving shape retainability
Soft-mix	Preventing whey from separating Improving mouthfeel

β -linkages. Generally those of high molecular weight form viscous solutions with the viscosity increasing with increasing molecular weight, while those of lower molecular weight show gel-like behavior, with some types of β -glucan able to form soft thermoreversible gels. Their major uses in foods to date have been as texturizing agents, especially as replacements for all or part of the fats in a range of dairy and bakery products, but there is also interest in including them in foods solely for their perceived health benefits.

β -Glucan and grains containing high levels of β -glucan have a useful physiological role as a dietary component and a significant part of research on β -glucans has focused on this aspect. For coronary heart disease, a leading cause of death in industrialized countries, high serum cholesterol levels and high levels of LDL (low density lipoproteins) cholesterol appear to be one of the risk factors. Consumption of foods rich in β -glucans significantly reduces

serum cholesterol levels and LDL cholesterol. The FDA, recognizing the benefit of β -glucans in the diet, has allowed the health claims for foods that contain more than 0.75 g of oat derived β -glucan for each serving portion. Other health benefits of diet rich in β -glucans include moderating the glycemic response to the digestion of starchy foods and lowering serum lipids levels. β -Glucans are also a source of soluble fiber because humans produce no β -glucan degrading enzymes and they are therefore not hydrolyzed in the small intestines. They are degraded by microbial fermentation in the large intestines. The fermentation produces beneficial short-chain fatty acids which appear to have a role in guarding against colo-rectal cancer.

The health benefits of β -glucan has stimulated interest in including β -glucan in food products. Normally, cereal grains do not contain high enough levels of β -glucan to provide the most desirable intake of soluble fiber. So there has been interest in obtaining enriched sources of β -glucan either through supplementation with extracted β -glucan or using cereal flours or brans enriched in β -glucan. For this type of use any functionality that the β -glucan may impart to the food as a hydrocolloid is minor and the major reason for including the flour or bran is because of the perceived health benefits.

β -Glucan has been extracted commercially, mainly from oats, but the extraction process is expensive so that the addition of the β -glucan extract to foods has been uneconomic. Since the early 1990s there have been several key developments that should see the extensive use of significant amounts of β -glucan in processed foods, not only on account of their previously perceived health benefits, but also because the β -glucan itself imparts significant functionality to the food, that is, it is a useful food hydrocolloid in its own right. And the major functionality that they have in processed foods, that is the replacement of fats, is a considerable health benefit, since the average western diet is overloaded with calories and too little fiber.

7.4 Dietary fiber – in health and disease

The Vahouny Symposia which have been held since 1981 have made an enormous contribution to our knowledge of the action of dietary fiber in foods. Reference will be made here to information from the 7th International Symposium published in the *Proceedings of the Nutritional Society* (2003, Volume 62, No. 1), from which further reading can be obtained.

7.4.1 Methods of measuring dietary fiber

Since no single scientific definition of dietary fiber is universally recognized, the methods of measurement are similarly in a state of flux. It is clear that the importance of non-digestible oligosaccharides (NDO) as dietary fiber components, based on their physiological behavior, has been recognized.

There are both soluble and non-soluble dietary fiber, such as cellulose and the soluble hydrocolloids which have been described above. To these should also be added the fructo-oligosaccharides and inulin, which can be extracted from chicory and Jerusalem artichoke on an industrial scale. High levels are also found in onion and leaf tissue of many grasses.

Two types of dietary fiber methodology are required: enzymic gravimetric for food labelling and control purposes and enzymic chemical for research purposes. These methods must yield similar dietary fiber results. The combination of Association of Official Analytical Chemists (AOAC) methods (2000) 985.29 and 991.43 (total dietary fiber) and the Uppsala enzymic chemical method (AOAM 2000 method 994.13) form a basis for fulfilling these requirements.

7.4.2 Colonic diverticula

Martin Eastwood has made a fundamental contribution to this subject through his work. Diverticulosis is a condition that is associated with aging. The older the person, the more likely they are to have diverticulosis. Diverticula are a herniation through the wall of the sigmoid colon and are likely to be a consequence of intracolonic pressure consequent to a low dietary fiber intake. The findings of Dr Eastwood show that a high-fiber diet from birth and preferably a maternal high-fiber diet lessens the risk of diverticulosis with age.

7.4.3 Anti-cancer effects of butyrate

Butyrate is an abundant material in colonic contents. As with the other short-chain fatty acids (acetate and propionate) butyrate is an end-product of bacterial fermentation of carbohydrates which have escaped digestion in the small bowel. Epidemiological evidence suggests that a high intake of dietary fiber protects against colo-rectal cancer. The mechanism underlying this protection are thought to be mediated by the short-chain fatty acid butyrate.

7.5 The appropriate molecular features to achieve Effective colon performance

Plantago ovata or *P. espaghula* (Plantaginaceae) is native to the Canary Islands and the Mediterranean regions of Southern Europe and is also indigenous to the Indo-Pak subcontinent. Its seed husk (ispaghula) is a rich source of effective polysaccharide (dietary) fiber for promoting the healthy functioning of the colon. A factor in its physiological fiber behavior is its high viscosity and gel-like character in water. This in turn is related to the

molecular parameters associated with this extremely high molecular weight polysaccharide. This is now the basic material of commercial products for treating constipation and for promoting health in the colon. One of the main products is FYBOGEL (Reckitt Benchiser). It was, therefore, important to study the molecular features which are responsible for the effective action of this dietary fiber in the colon. We first studied the molecular parameters associated with the polysaccharide. Its behavior in water is unusual. Immediately it is suspended in water fine whiskers grow out of the solid within one minute. This behavior continues and the fibres grow with time until the solid has been converted, first into a soft and then into a stiff gel. It is this interaction with water which controls the rheological behavior of this polysaccharide which in turn is partly responsible for its effectiveness in increasing stool bulk and decreases stool transit time. There are, however, *in vivo* changes and modifications, which occur after exposure to the fermentation activity of the colonic microflora. To mimic this behavior controlled degradation studies were undertaken which studied the effects on rheological performance. The objective is to follow the breakdown of the tertiary matrix via the gel into the water soluble state and evaluate how this progression might relate to its functionality within the colon and lead to the various physiological benefits which have been reported.

The investigation showed that the ispaghula husk matrix is capable of interacting with water to yield a viscoelastic system which is capable of being preserved throughout its transit through the colon. This arises because the solid matrix can interact with water to give a gel fraction and a completely soluble fraction capable of rapid fermentation to yield short-chain fatty acids. In turn, these physical and chemical states can initiate a sequence of physical and physiological processes during transit through the colon, which enable a product such as Fybogel to be an effective aid to color health.

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