Chapter 3
Materials for Encapsulation

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Abbreviations

Chemical Names

CMC	Carboxymethyl cellulose
EMC	Ethyl methylcellulose
GA	Gum arabic
GG	Gellan gum
GK	Gum karaya
GT	Gum tragacanth
HEC	Hydroxyethyl cellulose
HPC	Hydroxypropyl cellulose
HPMC	Hydroxypropyl methylcellulose
LBG	Locust bean gum
MC	Methylcellulose
MG	Mesquite gum
PVP	Polyvinylpyrrolidone
SSPS	Soluble soybean polysaccharide

Organizations/Services

CAS	Chemical Abstract Service

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EFSA	European Food Safety Authority
FAO	Food and Agriculture Organization
FDA	Food and Drug Administration (US)
JECFA	Joint Expert Committee Food and Agriculture
SCF	Scientific Committee on Food
WHO	World Health Organization
Characteristics	
ADI	Acceptable daily intake
DA	Degree of acetylation
DE	Degree of esterification
DE	Dextrose equivalent
DP	Degree of polymerization
DR	Degree of reaction
DS	Degree of substitution
GRAS	Generally recognized as safe
GSFA	General standards for food additives
HM	High methoxylated
LM	Low methoxylated
MM	Molar mass
MMD	Molar mass distribution
WHO	World Health Organization

3.1 Introduction

A multitude of substances are known which can be used to entrap, coat, or encapsulate solids, liquids, or gases of different types, origins, and properties. However, only a limited number thereof have been certified for food applications as "generally recognized as safe" (GRAS) materials. It is worth mentioning that the regulations for food additives are much stricter than for pharmaceuticals or cosmetics. Consequently, some compounds, which are widely accepted for drug encapsulation, have not been approved for use in the food industry. Moreover, different regulations can exist for different continents, economies, or countries, a problem which has to be addressed by food producers who wish to export their products or who intend expanding their markets.

The aim of this chapter is to present and update the existing knowledge about materials either already in use or of potential use in the encapsulation of various ingredients or additives used by the food industry. This chapter summarizes the materials, their chemical and physical properties, as well as the principal methods available to measure and analyze these properties. It is further intended to outline some of the basic chemistry which facilitates the selection of the most appropriate materials for the encapsulation of a specific compound by a suitable technology. To a certain degree, some studies performed on specific encapsulation projects will be reviewed. The chapter will not deal with analyses of the economics involved and will not describe specific technologies. It will, however, refer to the legislation on food additives.

There are already a number of excellent books and abundant publications dealing comprehensively with biopolymers, polysaccharides, hydrocolloids, or gums, and their use in the food industry. Nevertheless, the correlation of data on materials with specific requirements for microencapsulation is limited. The requirement to improve this correlation is patently clear from the conclusions of three seminal reviews published in 1991, 1999, and 2005 dedicated to microencapsulation in the food industry (Jackson and Lee 1991; Gibbs et al. 1999; Desai and Park 2005a).

"Although microencapsulation has found applications in the food industry the technology remains far from being fully exploited… Exciting new techniques such as cocrystallization and liposome formation will improve the number and quality of encapsulated ingredients. Although cyclodextrins are discovered many years ago, their potential for flavor encapsulation was realized only recently. Cyclodextrins provide exceptional stability to oxidation and evaporative losses. Due to cost reduction and imminent FDA approval, cyclodextrins will likely find widespread use in foods." (Jackson and Lee 1991).

"Numerous developments have been made in the field of encapsulated food ingredients…. Limitations in many of the encapsulation techniques have occurred due to high cost of production and the lack of food-grade available materials. Research is necessary to eliminate these limitations. Encapsulation currently is an art that is difficult for the food scientist to master. The food scientist does not have the information available in databases to enable him to make informed choices concerning the most appropriate material and encapsulation process. For example, the appropriate blends of starches and maltodextrins as encapsulation material could prove highly beneficial. The development of cyclodextrins has led to new products with longer shelf-life, reduced volatility, and protection of heat-labile substances. Preliminary indications are that liposomes have many benefits for the food industry including protection of materials until desired release or delivery. There is a great deal of research that needs to be done concerning the use of liposomes in the food industry. Unlike the pharmaceutical industry, which can tolerate high costs, manufacturing costs will have to be reduced for food applications." (Gibbs et al. 1999).

"The use of microencapsulated food ingredients for controlled-release applications is a promising alternative to solve the major problem of food ingredients faced by food industries. The challenges are to select the appropriate microencapsulation technique and encapsulation material. Despite the wide range of encapsulated products that have been developed, manufactured, and successfully marketed in the pharmaceutical and cosmetic industries, microencapsulation has found a comparatively much smaller market in the food industry. The technology is still far from fully developed and has yet to become a conventional tool in the food technologist's repertoire for several reasons….development time is rather long…requires multidisciplinary cooperation…low margins…relative inertia of well-established corporations…understanding of the industrial constrains…" (Desai and Park 2005a).

The majority of materials used for microencapsulation in the food sector are biomolecules. In addition to carbohydrate polymers/polysaccharides, which are the most abundant of the four major classes of biomolecules, proteins and lipids are also biomolecules suitable for microencapsulation in the food sector. Dealing with the nomenclature of carbohydrates would by far exceed the purpose of this

Table 3.1 Materials suited for microencapsulation in the food industry

Origin	Carbohydrate polymer	Protein	Lipid
Plant	Starch – Derivatives Cellulose – Derivatives Plant exudates – Gum arabic – Gum karaya – Mesquite gum Plant extracts – Galactomannans – Soluble soybean Polysaccharide	Gluten (corn) Isolates (pea, soy)	Fatty acids/alcohols Glycerides Waxes Phospholipids
Marine	Carrageenan Alginate		
Microbial/animal	Xanthan Gellan Dextran Chitosan	Caseins Whey proteins Gelatin	Fatty acids/alcohols Glycerides Waxes Phospholipids (Shellac)

chapter. The chapter, therefore, refers the reader to the appropriate IUPAC publications (IUPAC-IUB 1980). Table 3.1 lists groups of biomolecules, arranged according to their origin, which are found to be most suitable either when used alone or when used in combination with others for microencapsulation in the food industry. These will be the major topic of this chapter. In addition, a few other compounds such as poly(vinylpyrrolidone) and inorganic molecules will be considered.

3.2 Materials

3.2.1 Carbohydrate Polymers

Carbohydrates comprise more than 90% of the dry mass of all biomass and more than 90% thereof are carbohydrate polymers – polysaccharides. These natural homo- and copolymers are composed of sugar residues and/or their derivatives. Many native polysaccharides contain a small percentage of peptide residues remaining from their biosynthesis. However, these are normally removed during processing. Native polysaccharides are of enormous varieties. Moreover, they also form valuable sources for chemically modified materials, thus expanding their applicability and usefulness. Overall, polysaccharides are of tremendous economical importance. Their world consumption – with one of the main sectors being food – exceeds by far, for example, the production of all synthetic polymers.

Different protocols for the classification/designation of carbohydrate polymers can be found in the literature. Sometimes, however, these protocols are not consistent and

a combination of the classification related to the chemical structure and those related to the physical behavior exist. In particular, the designation as a "hydrocolloid" or a "gum" is not uniformly applied. Some authors use the terms as synonyms. Others understand gums as a subgroup of hydrocolloids. The names carbohydrate polymer and polysaccharide refer to the chemical structure; the designation as gum or hydrocolloid refers to the property that these polysaccharides hydrate in hot or cold water to form viscous solutions or dispersions at low concentration.

Overall, there are gums/hydrocolloids obtained by the chemical modification of native polysaccharides and others "harvested" from nature. The first group

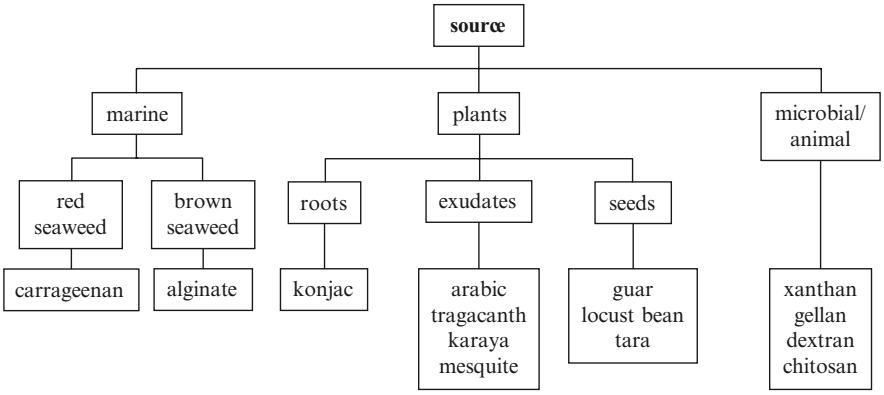

Fig. 3.1 Classification of natural carbohydrate polymers related to the source

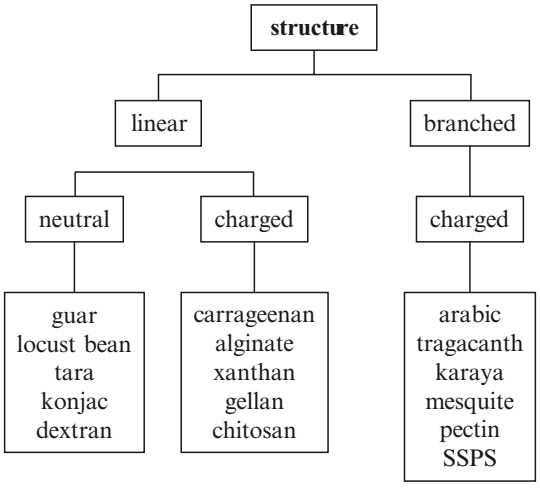

Fig. 3.2 Classification of carbohydrate polymers related to structural characteristics (Substances with only short side chains are considered here as principally linear. *SSPS* soluble soybean polysaccharide)

comprises derivatives of starch and cellulose. The second group includes a number of complex macromolecular structures such as plant exudates. Figure 3.1 presents a more detailed classification of natural food-grade materials with specification of their origin. Figure 3.2 provides the structural information. Carbohydrate polymers of both groups are subject of the subsequent sections.

3.2.1.1 Starch and Starch Derivatives

Chemical Description of Starch. (CAS# 9005-25-8) The polysaccharide starch is a polymer of α-D-glucose with the general chemical constitution $(C_6H_{10}O_5)_n$. Starch consists of two constitutionally identical but architecturally different polysaccharide molecules. These are essentially the linear amylose and the highly branched amylopectin. Normally, the amylose content is in the range of 20–30%, whereas the proportion of amylopectin is approximately 70–80%. The structure and composition varies with the source of the starch.

Amylose. (CAS# 2595-98-4) Figure 3.3 shows the principal chemical structure of amylose, poly[α-(1→4) anhydro-D-glucopyranose], consisting of almost exclusively linear molecules with α-(1→4)-linked D-glucose units, typically in the range 500–6,000 (Murphy 2000), forming a helix. The molar mass with a relatively narrow molar mass distribution depends on the botanical origin and the age of the plants, and also on the isolation procedure and technology. The measured molar mass can also depend on the sample preparation and the solubilization procedure used for the molar mass characterization. Some references even report molar masses up to one million (Parker and Ring 2001).

Amylopectin. (CAS# 9037-22-3) The principal structure of amylopectin molecules is shown in Fig. 3.4, side chains of about 30 D-glucose units are bonded with α-(1→6) linkages non-randomly at approximately every 20 to 30 glucose units along the chain. One amylopectin molecule may contain up to two million D-glucose units which is equivalent to a molar mass of approximately 4×10^8 g/mol.

Physico-chemical Characteristics of Starch. Starch is normally a white powder. Depending on its source, it may be odorless and tasteless. It is insoluble in cold water, ethanol, and most common solvents. It is naturally found radially packed in small grains of different shape (spherical or lentil-shaped) for which different ranges of size have been reported: 5–900 μm (Elias 1992), 1–100 μm (Murphy 2000). The size distribution determines the swelling behavior. The granules have been

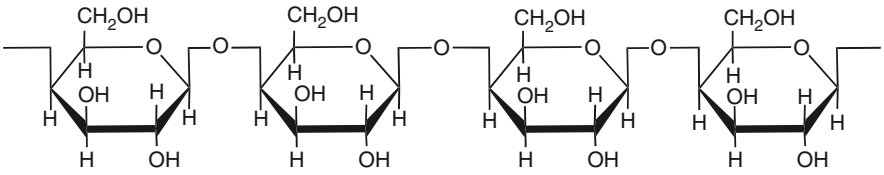

Fig. 3.3 Principal chemical structure of amylose

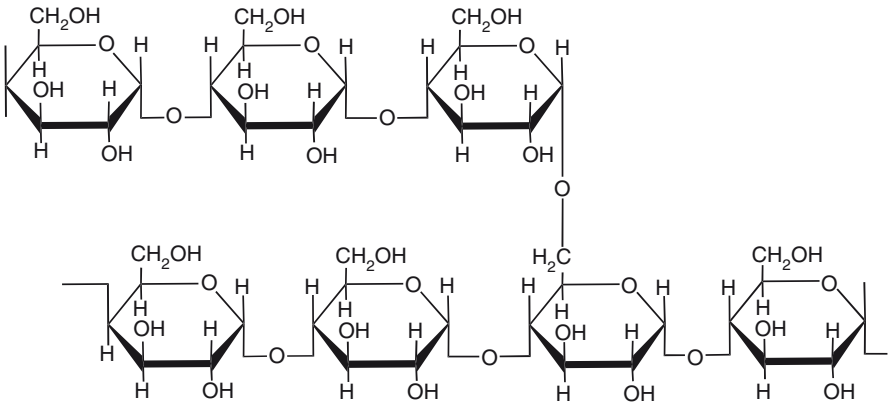

Fig. 3.4 Principal chemical structure of amylopectin

generally described as either larger and lenticular (lens-like, A-starch) or smaller and spherical (B-starch) (Ao and Jane 2007), with less swelling power. As the granules absorb water, they swell, lose crystallinity, and leach amylose. The higher the amylose content, the lower is the swelling power and the lower is the gel strength for the same starch concentration. However, a lower swelling power due to the high amylose content can be counteracted by a larger size of granule (Li and Yeh 2001; Singh et al. 2003; Chaplin 2007).

Both the amylose and amylopectin are complex macromolecules, with the capability of interacting intra- and intermolecularly to form ordered structures (Parker and Ring 2001). Amylose generally tends to wind up into a rather stiff left-handed single helix or forms even stiffer parallel left-handed double helical junction zones (Imberty et al. 1988). The helical structure is responsible for the specific solubility behavior. In starch, the amylose molecules are imbedded in a physical network of amylopectin molecules. This network prevents the amylose from forming a complete helical structure of the amylose.

Amylose has a very specific dissolution behavior. With hot water, amylose molecules dissolve as statistical coils of non-ordered segments and short helical parts whereas the amylopectin remains undissolved. In dilute solution, these short helical parts of the amylose grow relatively fast to longer helical parts, which organize laterally to form a double-stranded helix. Amylose slowly crystallizes from aqueous solution and becomes insoluble (retrogradation). During this process some of the water associated with the molecules is released. As a consequence, dried amyloses are no longer water soluble. In concentrated solutions of amylose, inter- and intramolecular association occurs with partial crystallization yielding a physical network – gelling of amylose (Elias 1992). The rate of retrogradation depends on the molar mass, concentration, temperature, and pH. The lower the temperature, concentration, and molar mass, the faster is the retrogradation. It is described as the fastest in the pH range 5–7, however, it can be retarded by salts (Rutenberg 1980).

The extended conformation of amylose causes the high viscosity of water-soluble starch and varies relatively little with temperature. Single helix amylose behaves

similarly to the cyclodextrins. It has a relatively hydrophobic inner surface that holds water molecules, and these can be easily replaced with hydrophobic lipid or aroma molecules (Chaplin 2007).

The amylopectin molecules are oriented radially in the starch granule. As the radius increases so does the number of branches required to fill up the space, with the consequent formation of concentric regions of alternating amorphous and crystalline structure (Chaplin 2007). Some amylopectins (for example, from potato) have phosphate groups attached to some hydroxyl groups, which increase its hydrophilicity and swelling power. Intense stirring in cold water yields colloidal dispersions. Due to branching, no retrogradation and crystallization is observed. Amorphous powders are obtained by drying, which may be redispersed easily in water and do not really form gels.

Origin and Isolation of Starch. Starch is stored most abundantly in tubers, roots, seeds, and fruits, but can also be stored in leaves, stems, and pollen grains. It is usually possible to identify the plant source by the microscopic examination of grains (Buléon et al. 1998). Each grain typically contains several million amylopectin molecules and a much larger number of amylose molecules.

Starch is the second most abundant polysaccharide after cellulose. The sources and commercial isolation are shown in Fig. 3.5. Starch is supplied as comparably low cost products of controlled quality and ready availability. Pure amylopectin can be isolated from "waxy" maize starch whereas amylose is best isolated subsequent to specific hydrolysis of the amylopectin with pullulanase (Vorwerg et al. 2002). Genetic modification of starch crops has recently led to starches with both improved and targeted functionality (Jobling 2004; Chaplin 2007).

Starch Derivatives (Wurzburg 1995, 2006). Chemical, biochemical, and physical modifications of starch are known. Many functional derivatives of starch are marketed including cross-linked, oxidized, acetylated, hydroxypropylated, and partially hydrolyzed molecules. The aim of starch modification is to alter the structure and affect the hydrogen bonding in a controllable manner in order to enhance and extend the industrial applicability.

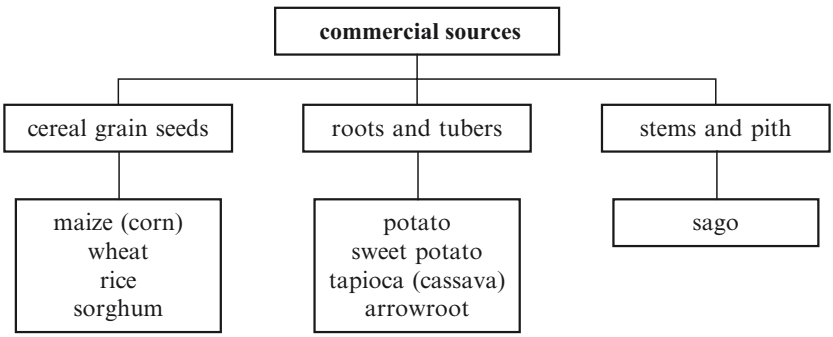

Fig. 3.5 Commercial sources of starch

Cross-linking replaces a limited number of hydrogen bonds between starch chains by permanent covalent bonds. As a result, swelling is inhibited and the starch offers higher heat and shear stability. In combination with the stabilization by introducing bulky groups, the shelf life can be improved. The starches modified in this way exhibit better tolerance to temperature fluctuations. Retrogradation can be prevented.

Hydrolysis (Blanchard and Katz 1995, 2006) is performed using 4 acids (chemical modification) or enzymes (selective biochemical modification) as catalysts. The resulting derivatives are assigned a Dextrose Equivalent (DE) value, which represents the degree of hydrolysis. Figure 3.6 illustrates a classification based on the DE.

Maltodextrins. (CAS# 9050-36-6) Maltodextrins are hydrolysates with a DE < 20. They are creamy white hygroscopic polysaccharide powders, which are almost tasteless or only moderately sweet and easily digestible. In the US usually corn or potato starch is used for the modification whereas in Europe it is commonly wheat. The source of maltodextrins is important for coeliacs since the wheat-derived maltodextrin can contain traces of gluten. Overall, maltodextrin is an acid- or enzyme-catalyzed starch hydrolysate with M_w < 4,000 g/mol.

Syrups. (CAS# 8029-43-4) Starch hydrolysates with a DE > 20 are further subdivided into four corn syrup types (Fig. 3.4). These differ by their sweetness, which increases from type 1 to type 4 (Critical Data Tables 1975).

Dextrins. (CAS# 9004-53-9) The term dextrin, in its broadest sense, may refer to any product obtained by any method (e.g., heat, acid, enzyme) for degrading the starch. The physical properties of dextrins can cover a very wide range. A synonym used for dextrins is starch gums. The tensile strength of dextrin film is lower than that for starch and decreases with the degree of conversion. However, dextrin formulations can be prepared at higher concentrations than unmodified starch yielding films with higher proportions of solids, which dry faster and are thicker.

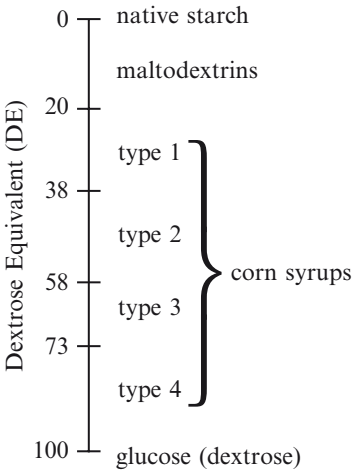

Fig. 3.6 Classification of starch hydrolysates based on the dextrose equivalent (DE) value

As an example, yellow corn dextrin is used to encapsulate water-insoluble flavors and oils by spray-drying (Wurzburg 2006).

Cyclodextrin. (CAS# 12619-70-4) Cyclodextrins are a family of cyclic oligosaccharides. Degradation of amylose, amylopectin, or glycogen by diluted acids or by enzymes of, e.g., *Bacillus macerans* yields these cyclic dextrins, which are non-branched oligomeric cycloamyloses composed of α-(1→4)D-glucopyranoside units. The ring structure results from the helical segments of the polysaccharide. Typical cyclodextrins contain six to eight glucose monomer units. The rings are cone-shaped with a cavity depth of 0.7–0.8 nm. However, much larger rings have also been derived. Figure 3.7a–c shows the chemical structures for typical cyclodextrins. They are denoted as follows (Szejtli 1998):

– α-cyclodextrin (CAS# 10016-20-3): six-sugar ring molecule, inner diameter 0.5 nm
– β-cyclodextrin (CAS# 7585-39-9) seven-sugar ring molecule, inner diameter 0.6 nm
– γ-cyclodextrin (CAS# 17465-86-0) eight-sugar ring molecule; inner diameter 0.8 nm

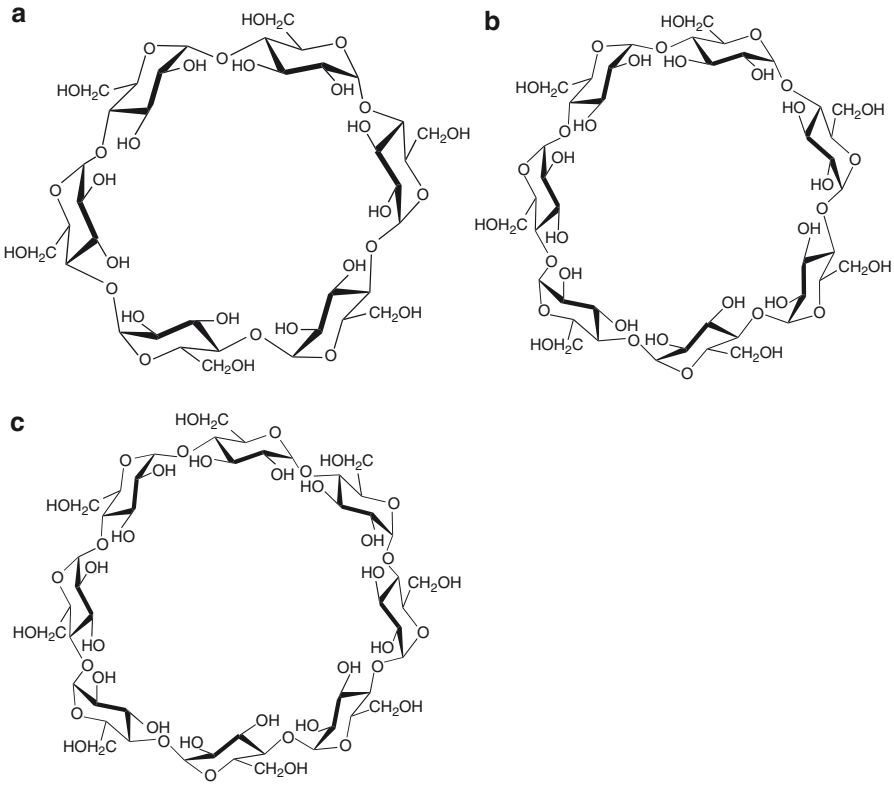

Fig. 3.7 Chemical structure of cyclodextrins. (**a**) α-cyclodextrin, (**b**) β-cyclodextrin, (**c**) γ-cyclodextrin

Cyclodextrins form inclusion complexes (Reineccius et al. 2005; see also Sect. 2.3.10). Their solubility in water at 25°C differs considerably, with γ-cyclodextrin being the best soluble (23.2 g/100 ml) followed by α-cyclodextrin (14.5 g/100 ml) and β-cyclodextrin (1.85 g/100 ml) (Blanchard and Katz, 2006).

Cyclodextrins are not adsorbed in the upper gastrointestinal tract. They are completely metabolized by the colon microflora (Szente and Szejtli 2004).

Polydextrose. It is also designated as (poly-D-glucose). It is a synthetic, highly branched polymer with many types of glycosidic linkages created by heating dextrose with an acid catalyst (acid-catalyzed condensation) and purifying the resulting water-soluble polymer. For example, melt-condensation of 89% D-glycose (dextrose), 10% sorbitol (D-glucitol), and 1% citric acid results in statistically branched polydextrose with primarily 1→6 linkage and molar masses up to 22,000 g/mol, which is water-soluble (Elias 1992). Polydextrose is preferably used as a bulking agent because it is tasteless and is similar to fiber in terms of its resistance to digestion.

Modified starch and maltodextrin have been used for coating and encapsulation by several technologies including spray-drying, fluidized bed spray-drying, fluidized bed granulation, compacting, and most importantly extrusion. Molecular inclusion is possible with cyclodextrins. Maltodextrins are cheaper than gum arabic and are, therefore, in some cases recommended as a partial substitute in encapsulation (Shahidi and Regg 1991).

3.2.1.2 Cellulose and Cellulose Derivatives

Chemical Description of Cellulose. (CAS# 9004-39-1) Cellulose (Coffey et al. 1995, 2006) is a polymer of β-D-glucose. The chain units are linked by β-(1→4)-glycosidic bonds. In contrast to starch, where all -CH_2OH groups are oriented along the same side of the molecular plane, the –CH_2OH groups in cellulose are oriented alternating above and below the plane thus producing long linear chains as is demonstrated in Fig. 3.8. Due to the absence of side chains, cellulose molecules can arrange close together and form rigid structures.

Only a few cellulose molecules are pure poly(β-(1→4)-glucopyranoses). The majority contains a low percentage of several other glucose units. As an example, cotton contains approximately 1.5% xylose as well as smaller amounts of mannose, galactose, and arabinose. Further, approximately one –COOH group per 500–1,000 glucose units can be found in native cellulose. These hydroxyl groups can react with acids to form esters and with alcohols to form ethers. Dependent on the origin, the degree of polymerization is in the range of 1,000–8,000 (Murray 2000), with a narrow molar mass distribution. Micro-crystalline cellulose is composed of 100–300 glucose units.

Physico-chemical Characteristics of Cellulose. Cellulose is insoluble in water and other ordinary solvents. It is a stiff polymer with an extended rod-like conformation. In microfibrils, the multiple hydroxyl groups on the glucose residues bond with each other, holding the chains firmly together. In contrast to starch, cellulose is

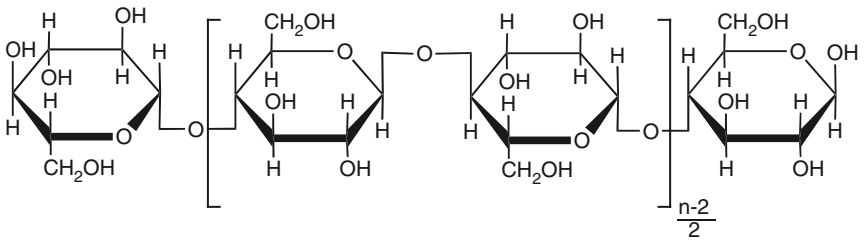

Fig. 3.8 Principal chemical structure of cellulose

much more crystalline. Whereas starch undergoes a crystalline to amorphous transition at 60–70°C in water, cellulose requires 320°C and 25 MPa to become amorphous in water (Chaplin 2007).

Origin and Isolation of Cellulose. Cellulose is the major structural material of plants. It is considered as the most abundant organic substance existing on the Earth. The primary cell wall of green plants is made of cellulose. Wood is largely cellulose, and cotton is almost (91%) pure cellulose. Other important natural sources are flax, hemp, jute, and straw. Acetic acid bacteria are also known to synthesize cellulose, as well as many forms of algae.

Derivatives of Cellulose. The hydroxyl groups of cellulose can partially or completely react with various reagents to produce derivatives with properties desired and/or required for food applications. Raw material used for the modification is cellulose pulp obtained from wood pulp or from cotton linters, the short fibers of cotton. The intended properties of the derivatives govern the selection of the raw material type. Theoretically, all three hydroxyl groups of the anhydroglucose unit can be subject to substitution. Cellulose ethers are the most important cellulose derivatives for food applications. Due to the limited solubility of cellulose, the majority of chemical modifications are performed in the heterogeneous media. Products with different degrees of substitution (DS) are obtained. The DS describes the average number of substituted hydroxy groups per sugar unit. Consequently, the maximum DS is three. GRAS cellulose ethers are summarized in Table 3.2. Selected structures are presented in Fig. 3.9.

Overall, the ultimate properties of modified cellulose depend on the substituent type, its frequency, and distribution along the polymer backbone, the molar mass, and the molar mass distribution. Practically, also the bulk properties, granular or powdered, can have an impact, for example, on the solution properties. In general, aqueous solutions of modified celluloses are odorless, colorless, and clear. Due to their capability of absorbing water appropriately to the relative humidity, storage without contact to humidity is strongly recommended.

Methylcellulose (MC). MC (Fig. 3.9a) is a hydrophilic white powder, which dissolves in cold water forming a clear viscous solution. Both the higher DS and the degree

Table 3.2 Food grade (GRAS) cellulose derivatives

Modification	CAS	E	DS[a] or DR[b]
Non	9004-39-1	460	
Methyl	9004-67-5	461	DS 1.3–2.6
Ethyl	9004-57-3	462	DS 2.1–2.6
Hydroxypropyl	9004-64-2	463	DR 4
Hydroxypropyl methyl	9004-65-3	464	DS (methyl) 0.9–1.8 DR (HP) 0.1–1.0
Ethyl methyl	9004-69-7	465	
Carboxy methyl (Na)	9004-32-4	466	DS 0.4–1.4
Ethyl hydroxyethyl	9004-58-4	467	
Crosslinked CMC	74811-65-7	468	

[a]*DS* Degree of substitution – average number of substituted hydroxyl groups per saccharide unit; different information from different sources, widest range taken
[b]*DR* Degree of reaction – average number of reagent molecules reacted with one saccharide unit

of polymerization (DP) result in lower solubility. The viscosity of MC solutions is reasonably stable over a wide pH range, pH 3–11. Three-dimensional gel formation occurs on heating above 50°C. MC of higher DS has a lower gelation temperature. The gels are reversible on cooling; however, a pronounced hysteresis is typical between heating and cooling. MC has good film forming properties and to a certain extent, surface activity. It is not digestible. The synthesis steps include heating of raw cellulose with NaOH and treatment with methyl chloride.

Hydroxypropyl methyl cellulose (HPMC). HPMC (Fig. 3.9b) is very similar to MC. It is supplied as white to off-white powder or granules, which swell and dissolve in water to form a viscous, non-ionic colloidal solution. It is also soluble in most polar solvents. Aqueous solutions are surface active and form films upon drying. They undergo reversible transformation from sol to gel upon heating and cooling, designated as reversible thermal gelation. However, the gel transition temperature depends on the ratio of methyl to hydroxypropyl derivatization. It can shift from 50 to 90°C. Moreover, the gel texture also changes with increasing hydroxypropyl substitution. In addition, the total DS influences the solubility. Typically, HPMC has a molar mass higher than 10,000 g/mol, $T_m = 220$°C, and a density of 1.6 g/ml (Greminger and Krumel 1980).

The solutions of both MC and HPMC exhibit pseudoplastic non-thixotropic flow properties, which are not a function of the DS within the range of commercial products. Deviation from the Newtonian behavior increases with the molar mass. Importantly, since flow properties are dependent on the molar mass and the molar mass distribution of the macromolecular substance, a blend of high and low molar mass polymers can have different flow properties compared to a polymer having the same solution viscosity as the blend but having a narrow molar mass distribution. This holds for modified celluloses and also for other biopolymers. Concentrations as low as 0.001–1% are able to reduce the surface tension and the interfacial tension (Greminger and Krumel 1980).

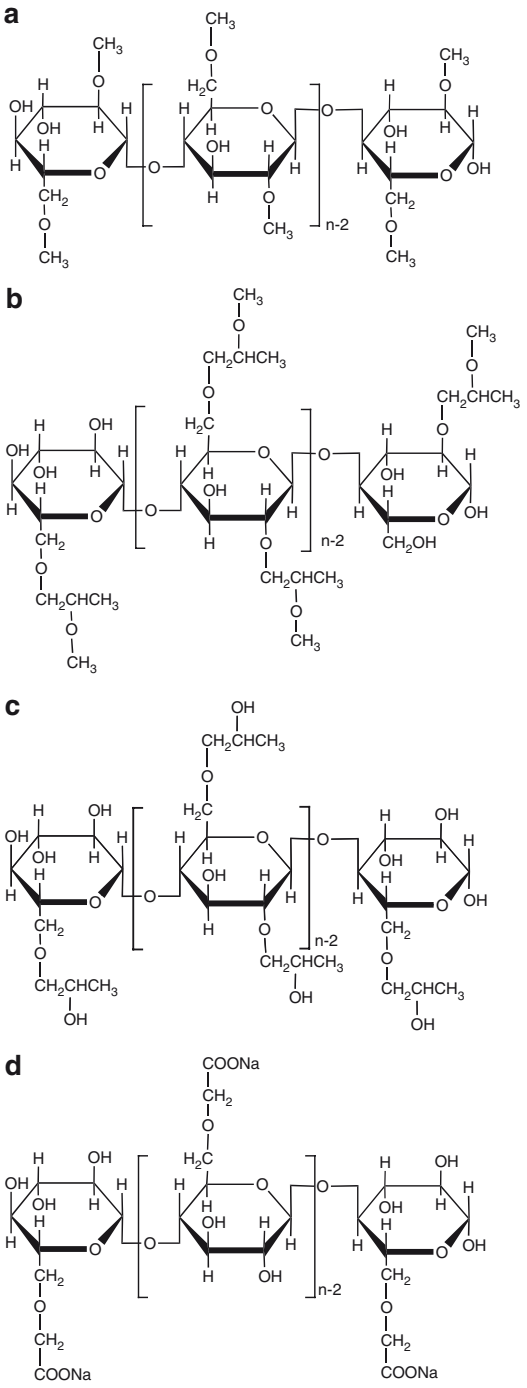

Fig. 3.9 Principal chemical structures of cellulose derivatives. (**a**) methyl (DS = 2), (**b**) methylhydroxypropyl, (**c**) hydroxypropyl, (**d**) carboxymethyl (DS = 1)

Hydroxypropyl cellulose (HPC). (Butler and Klug 1980; Picker-Freyer and Düring 2007) This non-ionic cellulose ether (Fig. 3.9c) is soluble in cold water. The viscosity of the solution can be adjusted by the degree of polymerization. Due to the presence of both the hydrophilic and hydrophobic groups, it becomes insoluble at temperatures above approximately 45°C. However, no gel is formed. Advantageous features include the solubility in ethanol and mixtures of ethanol and water, good film formation, and the high surface activity compared to most other hydrocolloids (Murray 2000). The films are flexible, glossy, and non-tacky (Butler and Klug 1980).

HPC is available in a wide range of molar mass from 6×10^4 to 1.2×10^6 g/mol. A high degree of reaction, DR = 4, enhances the resistance to both acid hydrolysis and biological degradation. HPC is compatible with a number of high molar mass, high-boiling waxes and oils and can, therefore, be used to modify the properties of these materials. The addition of HPC to wax or oil systems will increase the system viscosity and improve the hardness and crack resistance of coatings made thereof (Butler and Klug 1980). It is compatible with most water-soluble gums and resins, and yields homogeneous solutions with carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), MC, gelatin, sodium caseinate, poly(ethylene oxide), carbowax, guar, alginate, and locust bean gum. With anionic polymers such as CMC and alginate, a synergistic viscosity increase is obtained, whereas with non-ionic polymers such as HEC, MC, guar gum, a lower than expected viscosity is obtained (Butler and Klug 1980).

Ethyl methylcellulose (EMC). It behaves like MC and HPMC. It is soluble in cold water and forms gels on heating. More interesting is the surface activity since the gels are comparably weak.

Ethylcellulose (EC). This derivative is a water-insoluble commercial thermoplast used for coating and controlled release applications, $T_m = 135$°C.

Sodium carboxymethyl cellulose (CMC). CMC (Fig. 3.9d) is produced by reaction of cellulose with alkali and chloroacetic acid. The DP decreases slightly during the modification. The molar mass is typically in the range of 4×10^4–10^6 g/mol. The modification yields areas of high and low substitution. The purified product appears as a white to off-white, tasteless, odorless free-flowing powder.

CMC is an anionic linear polyelectrolyte, soluble in both cold and hot water. As typical for polyelectrolytes, the molecular conformation in aqueous solution strongly depends on the concentration, ionic strength, and pH. The polymer chains of CMC are most extended at low concentrations, low ionic strength, and high pH whereas with increasing concentration, ionic strength, and decreasing pH the molecules increasingly coil. At concentrations above the overlap concentration, thermo-reversible gels are formed in water. With heavy metals, three-valent cations, and the majority of polycation precipitation occurs. However, in the isoelectric range solubilization was observed with proteins such as soy protein and caseinate (Stelzer and Klug 1980).

CMC rapidly dissolves in cold water and gives clear and colorless solutions. The solution viscosity decreases during heating. Nevertheless, the solution behavior strongly depends on the molar mass and the DS. The more hydrophobic the lower

substituted CMCs are thixotropic, the more hydrophilic the higher substituted ones exhibit pseudoplastic behavior. At low pH, CMC may form cross-links through lactonization between carboxylic acid and free hydroxyl groups (Chaplin 2007; Kästner et al. 1997).

3.2.1.3 Plant Exudates and Extracts

Polysaccharide plant exudates and extracts are complex macromolecular substances. Some of them are mixtures consisting of oligomers and polymers of different chemical structure and/or chain architecture. Several of the materials used for food encapsulation are products of gummnosis and are also therefore named plant gums in practice.

Gummnosis is widespread in the plant kingdom. It is the result of stress conditions such as wound, heat, and drought. Gums produced in response to the injury of the plant form a barrier at the lesion hindering the invasion by microorganisms. Only a few plant species are cultivated at present to provide gums for the food industry. Most of them belong to the Leguminosae family. Some examples of plants with the appropriate gum harvested thereof are listed below:

- *Acacia senegal* – gum arabic (gum senegal)
- *Astragalus spp.* – gum tragacanth
- *Cyamopsis tetragonolobos* – guar gum
- *Ceratonia siliqua* – locust bean gum

However, a wide range of exudates from other trees and shrubs are also harvested and consumed in their countries of origin, such as mesquite gum (Orozco-Villafuerte et al. 2005). These gums are generally harvested from wild growing trees.

Gum Arabic

Chemical Description of Gum Arabic (GA). (CAS# 9000-01-5) Gum arabic is a complex mixture of arabinogalactan oligosaccharides, polysaccharides, and glycoproteins. It is a branched neutral or slightly acidic substance. The chemical composition and the composition of the mixture can vary with the source, climate, season, age of trees, rainfall, time of exudation, and other factors. The backbone has been identified to consist of β-(1→3)-linked D-galactopyranosyl units. The side chains are composed of two to five β-(1→3)-linked D-galactopyranosyl units, joined to the main chain by 1,6-linkages. Both the main and the side chain contain units of α-L-arabinofuranosyl, α-L-rhamnopyranosyl, β-D-glucuronopyranosyl, and 4-O-methyl-β-D-glucuronopyranosyl. The latter two usually occur preferably as end-units (Verbeken et al. 2003). Depending on the source, the glycan components of GA contain a greater proportion of L-arabinose relative to D-galactose (*Acacia seyal*) or D-galactose relative to L-arabinose (*Acacia senegal*). The gum from *Acacia seyal* also contains significantly more 4-O-methyl-D-glucuronic acid but less L-rhamnose

and unsubstituted D-glucuronic acid than that from *Acacia senegal* (Williams and Phillips 2000; Williams et al. 2006; Motlagh et al. 2006; Chaplin 2007).

GA has a complicated molar mass distribution. Some authors report a mixture of lower molar mass polysaccharide ($M_w \approx 2.5 \times 10^5$ for the major component) and higher molar mass hydroxyproline-rich glycoprotein ($M_w \approx 2.5 \times 10^6$ for the minor component) (Goodrum et al. 2000; Renard et al. 2006). Others describe three fractions: arabinogalactan (88.4%) with 3.8×10^5 g/mol, arabinogalactan-protein complex (10.4%) with 1.45×10^6 g/mol, and a low molar mass glycoprotein (1.2%) with 2.5×10^5 g/mol (Verbeken et al. 2003). Because it is a mixture, which varies with source, the exact chemical composition and molecular structures are still debated.

Physico-chemical Characteristics of Gum Arabic. Gum arabic is odorless, colorless, tasteless, and does not affect the odor, color, and taste of the system to which it is added. It is highly soluble in water and dissolves in both cold and hot water with concentrations up to 50 wt%. The solutions exhibit Newtonian behavior at concentrations up to 40 wt% and become pseudoplastic at higher concentration. The viscosity of solutions varies strongly with the GA type, pH, and ionic strength. Maximum viscosity is achieved between pH 6 and 7. GA acts as protective colloid and excellent emulsifier. The adhesive property is not related to the viscosity (Meer 1980a). However, and rather confusingly, the molecular aggregation can cause both shear thinning and time-dependent thickening behavior at low shear (Sanchez et al. 2002).

GA has the ability to create a strong protective film around oil droplets (Krishnan et al. 2005), which results from the highly branched arabinogalactan-protein structure containing both protein and polysaccharide moieties. The hydrophobic polypeptides anchor the polysaccharide onto the surface of the oil droplet and the hydrophilic carbohydrate chains prevent the aggregation by forming a thick charged layer. This is quite unique. Very few polysaccharide-protein systems have a stabilization mechanism comparable to GA (Nakamura et al. 2006; Kim and Morr 1996; Kim et al. 1996).

GA is compatible with most other plant hydrocolloids, proteins, carbohydrates, and modified starches. The viscosity of a solution of a mixture of GA and gum tragacanth tends to be lower than that of either constituent solution. Minimum solution viscosity was obtained for 80% gum tragacanth and 20% GA. Overall, when used as a fixative in the spray-drying of flavors, it forms a thin and impenetrable film around the flavor particle, protecting it from oxidation and evaporation and preventing it from absorbing moisture from the air (Meer 1980a; McNamee et al. 1998). GA was also found to be a useful prebiotic, which promotes beneficial physiological effects (Phillips et al. 2007).

Origin and Isolation of Gum Arabic. Gum arabic, also called gum acacia, is the oldest and best known of all natural plant gums. It is a dried exudate obtained from the stems and branches of *Acacia senegal* or *Acacia seyal* (FAO 1999). However, the name is also used for other gums produced by other *Acacia* species (Verbeken et al. 2003; FAO 1995). Despite there being more than 500 species of acacia trees, most commercial GA is produced from *Acacia senegal* and *Acacia seyal*, which are grown commercially throughout the Sahel from Senegal and Sudan to Somaliland.

Gum Tragacanth

Chemical Description of Gum Tragacanth. (CAS# 9000-65-1) Gum tragacanth is a complex mixture of highly branched, heterogeneous polysaccharides (Stauffer 1980). It occurs naturally as slightly acidic calcium, magnesium, or potassium salt with a molar mass of approximately 8.4×10^5 g/mol. Moreover, an elongated shape has been described with a length of 4,500 nm and a diameter of 19 nm (Gralen and Karrholm 1950). Gum tragacanth consists of two components: (a) a water-swellable component designated as bassorin, which contains the tragacanthic acid polymer with a molar mass of approximately 10^5 g/mol (Elias 1992), and (b) a water-soluble component, a colloidal hydrosol, tragacanthin with a molar mass of approximately 10^4 g/mol (Elias 1992). This is a neutral polysaccharide, which, at best, contains only small amounts (3%) of uronic acid (Aspinall and Baillie 1963) (sometimes there is confusion with the names). Due to the complexity of the substance, different molecular descriptions have been reported.

Depending on the source, the ratio of the water-swellable to the water-soluble fraction varies. Examples are 35:65 and 60:40. The tragacanthic acid fraction has a higher molar mass and a rod-like molecular shape (Stephen and Churms 1995). The main chain is formed by (1→4)-linked D-galactose residues with side chains of D-xylose units attached to the main chain by (1→3)-linkages. The water-soluble tragacanthin is a neutral, highly branched arabinogalactan with a spherical molecular shape. Its structure probably consists of a core composed of (1→6)- and (1→3)-linked D-galactose with attached chains of (1→2)-, (1→3)-, and (1→5)-linked L-arabinose (Verbeken et al. 2003; FAO 1995).

Physico-chemical Characteristics of Gum Tragacanth. Gum tragacanth is one of the most acid-resistant gums. It does not degrade at low pH. It is considered as a bifunctional emulsifier. First, it increases the viscosity of the aqueous phase and secondly it lowers the interfacial tension between the oil-in-water emulsion, and thus eliminates the need to incorporate surface-active agents. The suspending properties result from the negative charges. Gum tragacanth forms viscous aqueous solutions even at low concentration, which exhibits pseudoplastic flow properties. Similar to GA, it forms a protective film around oil droplets (Mohammadifar et al. 2006).

Origin and Isolation of Gum Tragacanth. Gum tragacanth is a dried exudate obtained from the stems and branches of *Astragalus gummifer* Labillardière and other Asiatic species of *Astragalus* (FAO 1992b). These plants grow in the highlands and deserts of Turkey, Iran, Iraq, Syria, Lebanon, Afghanistan, Pakistan, and Russia.

Gum Karaya

Chemical Description of Gum Karaya. (CAS# 9000-36-6) Gum karaya (Meer 1980b) is a complex, partially acetylated polysaccharide obtained as a calcium and magnesium salt. It has a branched structure and a molar mass up to 1.6×10^7 g/mol

has been reported (Le Cerf et al. 1990). The backbone consists of α-D-galacturonic acid and α-L-rhamnose residues. Side chains are attached by (1→2)-linkage of β-D-galactose or by (1→3)-linkage of β-D-guluronic acid to the galacturonic acid of the main chain. Furthermore, half of the rhamnose residues of the main chain are (1→4)-linked to β-D-galactose units (Weiping 2000).

Physico-chemical Characteristics of Gum Karaya. Powdered gum karaya is white to grayish white. It is one of the least soluble of the exudate gums. Only 10% of the native gum solubilizes in cold water, increasing to 30% in hot water. After deacetylation, 90% dissolves in water (Verbeken et al. 2003). Gum karaya is compatible with other plant hydrocolloids, proteins, and carbohydrates.

Origin and Isolation of Gum Karaya. Gum karaya, sometimes known as Sterculia gum, is a dried exudate from the stems and branches of *Sterculia urens* Roxbourg and other species of *Stericula* or from the species of *Cochlospermum* (FAO 1992a). India is the largest producer of gum karaya.

Mesquite Gum

Chemical Description of Mesquite Gum. Mesquite gum is the neutral salt of a complex acidic branched polysaccharide. Its backbone is formed by (1→3)-linked β-D-galactose residues with (1→6)-linked branches, bearing L-arabinose (pyranose and furanose ring forms), L-rhamnose, β-D-glucuronate, and 4-O-methyl-β-D-glucuronate as single sugar or oligosaccharide side chains. It also contains a small amount of protein (0.7–5.8%) (Orozco-Villafuerte et al. 2003; Anderson and Farquhar 1982; Anderson and Weiping 1989; Goycoolea et al. 1997; Vernon-Carter et al. 2000). There is some chemical similarity with gum arabic (Islam et al. 1997).

Physico-chemical Characteristics of Mesquite Gum. Mesquite gum has a level of solubility comparable to GA. The color of the clear solutions is brown, slightly darker than those from GA. Hydrophobic affinity chromatography yielded five fractions differing in their molar masses (3.5×10^4–9.3×10^5 g/mol) and protein content (0.04% to about 30%). The two major fractions with >90% have protein contents much lower than 1% (Orozco-Villafuerte et al. 2003).

Solutions of up to 50% can be prepared. However, the increase of the viscosity with increasing concentration is steeper for mesquite gum in comparison to GA (Goycoolea et al. 1995). Mesquite gum has good film formation properties (Diaz-Sobac et al. 2002).

Origin and Isolation of Mesquite Gum. This gum is obtained from the mesquite tree (*Prosopis spp.*) or shrub, which grows in the southwest of the USA, Mexico, and other areas of the world. It is preferably harvested for local use and limited commercialized for local markets. Despite similar or even partially better application properties compared to GA, it finds either no use or limited use in industrial applications. The main reason for not using the mesquite gum in industrial applications is that its supply cannot be guaranteed, as all the gum is collected from wild growing trees (Orozco-Villafuerte et al. 2005).

Galactomannans

Chemical Description of Galactomannans. Locust bean gum (LBG) (Gidley and Reid 2006) (CAS# 9000-40-2), also called carob bean gum, tara gum (CAS# 39300-88-4), and guar gum (CAS# 9000-30-0, 9000-30-3, 9066-07-3) are galactomannans. They consist of linearly (1→4)-linked β-D-mannopyranosyl units with single α-D-galactopyranosyl units connected by (1→6) linkages as side branches. The three gum types differ in the ratio of D-mannosyl to D-galactosyl. On average, in LBG every fourth main chain unit bears a side unit whereas in tara gum it is every third, and in guar gum every second main chain unit, Fig. 3.10. The actual ratios reported in the literature vary slightly and differ from the average. For LBG it is between about 3.9:1 and 3.5:1 (Hoefler 2004; Chaplin 2007). The ratio corresponds to galactose weight contents of 17–26% for LBG, 25% for tara gum, and 33–40% for guar gum (Wielinga 2000). However, the side units are highly unevenly distributed along the backbone. More block polymer arrangement than statistical distribution occurs.

Physico-chemical Characteristic of Galactomannans. The three gum types differ in their solubility. The solubility increases with increasing number of side units. While guar is fully water soluble at room temperature, the solubility of tara is about 70% under these conditions but is completely soluble above 70°C. LBG has a limited water solubility at ambient temperature. It swells below 60°C but becomes soluble above 60°C and fully hydrated if heated for 10 min at 80°C (Hoefler 2004; Seaman 1980). Average molar masses ranging from about 1.5×10^5 to 1.5×10^6 g/mol have been reported for guar gum, having higher molar masses and producing higher viscosities of solutions than LBG. However, the isolation process, purification, solution preparation, and characterization method can have an impact on the molar masses obtained (Picout et al. 2001; Picout et al. 2002; Patel et al. 2006). The solutions of all three gum types exhibit pseudoplastic behavior.

Origin and Isolation of Galactomannan. LBG, tara, and guar are isolated from the endosperm of the seeds of the carob tree (*Ceratonia siliqua*), the tara shrub (*Cesalpinia spinosa*), and the guar plant (*Cyamopsis tetragonoloba*), respectively.

Pectins

Chemical Description of Pectins. (CAS# 9000-69-5) Pectins (May 2000; Lopez da Silva and Rao 2006) are high molar mass hetero-polysaccharides with at least 65 wt% of α-(1→4)-linked D-galacturonic acid-based units. These units may be present as free acid, salt (sodium, potassium calcium, ammonium), naturally esterified with methanol, or as acid amid in amidated pectins. Furthermore, a range of neutral sugars such as L-rhamnose, D-galactose, L-arabinose, D-xylose, and small amounts of others are part of the polymer chain. L-rhamnose units exist exclusively as (1→2)-linked in the main chain, whereas all other neutral sugar residues are bond preferably at the rhamnose and galactose units to the main chain (Elias 1992). Pectins exhibit a very complex, non-random structure

with linear blocks of homo-poly(galacturonic acid), so-called smooth regions, and with highly branched blocks, so-called hairy regions (May 2000; Voragen et al. 1995).

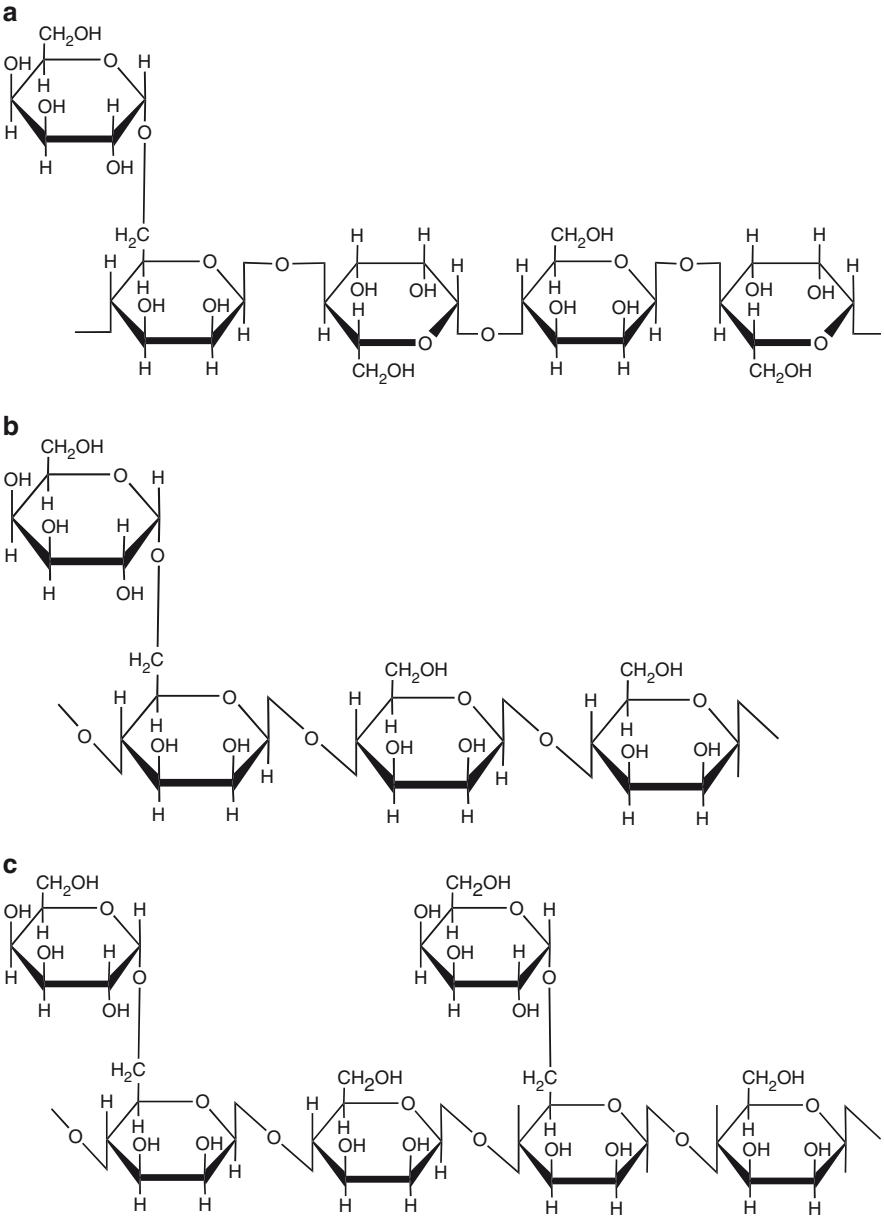

Fig. 3.10 Principal chemical structures of galactomannans. (**a**) locust bean gum, (**b**) tara gum, (**c**) guar gum

Pectins can differ by the degree of esterification of the carboxy groups of the galacturonic acid, which is in general in the range of 20–80%. Pectins with more than 50% esterification are designated as high-esterified (HM, high methoxylated) and distinguished from low-esterified pectins (LM, low methoxylated) with less than 50% ester groups. The molar mass depends on the pectin source and processing, and was reported to be in the range of 10^4–2×10^5 g/mol (Voragen et al. 1995). A small portion of the hydroxyl groups are acetylated in pectins from sugar beet, but not in those from citrus fruits.

Physico-chemical Characteristics of Pectins. Pectins are soluble in water but insoluble in most organic solvents. Aqueous solutions can be obtained up to concentrations between 6% and 12%, depending on the pectin type. The solutions have low viscosity compared to other plant gums. At low concentration, the rheological behavior is close to Newtonian behavior, but it shifts to pseudoplastic at higher concentration (Pedersen 1980).

Pectins are non-permanently negatively charged macromolecules and, therefore, behave as polyelectrolytes and their solution properties, and in particular gelation, are sensitive to pH variation and the presence of cations in the solution. Pectin solutions are most stable at pH 3–4 (Voragen et al. 1995). The gelation also depends on the nature and the quality of the raw material but primarily on the degree of esterification. Different gelation mechanisms have been identified for pectins with high methoxyl content (HM) and low (LM) methoxyl content. HM pectins gel only in the presence of sugars or other cosolutes in the low pH range, where the acid groups are not completely ionized. The gel strength increases with decreasing pH. The interaction between calcium ions and pectin governs the gelation of LM pectins and depends on the proportion and arrangement of the carboxyl groups in the pectin chain. The reactivity increases with decreasing degree of esterification. The presence of amide groups extends the range of the calcium ion concentration where the LM pectin forms gels.

Origin and Isolation of Pectins. Biologically, pectins serve as a kind of cement for the cell wall in higher plants. They are present in fruits in variable amounts and qualities. The main pectin producers are located in citrus fruit producing areas in Europe and Latin America, where the pectins are isolated from the citrus peel, orange peel, and residues from the extraction of citrus juice, citrus oil, and apple juice. Hot aqueous mineral acid is used to extract the raw material with the objective of obtaining pectins of high molar mass at high concentration. Pectins of a wide range of types are offered in the market.

Soluble Soybean Polysaccharide

Chemical Description of Soluble Soybean Polysaccharide. Soluble soybean polysaccharide (SSPS) is mainly composed of galactose, arabinose, and galacturonic acid, but the chain also contains many sugars at low quantities including rhamnose, glucose, xylose, and fucose. The exact structure is not fully understood. An average molar mass of several hundred thousand has been reported, though three components

varying in their molar mass have also been identified (Nakamura et al. 2000). The negative charges, i.e., the galacturonic acid units, are located on the main backbone chain, whereas the shorter side chains contain neutral sugar units.

Physico-chemical Characteristics of Soluble Soybean Polysaccharide. Due to the negative charges in the backbone, SSPS is considered as an anionic polyelectrolyte. SSPS is soluble in both cold and hot water yielding solutions of relatively low viscosity. For comparable concentrations, the viscosity is considerably lower than that for guar gum or HM pectin, but up to concentrations of 30 wt% it is found to be higher than that for gum arabic. SSPS solutions do not gel. Moreover, the viscosity is only slightly affected by heat, salt, or by acidic pH variation (Furuta and Maeda 1999).

The adhesive and film forming properties of SSPS are excellent. Films processed without any additives show high resistance to tension. The films are generally colorless, transparent, water soluble, and edible and are suitable for coating the surfaces of food and food ingredients. SSPS can prevent oxidation of oils (Maeda 2000). SSPS has the ability to stabilize protein particles at low pH without increasing the viscosity. It can be used as an emulsifier and as a stabilizer for emulsions.

Origin and Isolation of Soluble Soybean Polysaccharide. SSPS is extracted from okara, the residue after oil and soy protein extraction from soybean (Maeda 2000). It is obtained as a powder of several varieties, which can be tailored for specific applications.

3.2.1.4 Marine Extracts

Seaweed can be regarded as another almost unlimited source of different types of polysaccharides for many industrial applications. Some of them have been found to be useful for encapsulation in the food sector.

Carrageenans

Chemical Description of Carrageenans. (CAS# 9000-07-1) Carrageenans (Guiseley et al. 1980; Piculell 1995, 2006; Imeson 2007) are a family of high molar mass sulfated polysaccharides, for which the individual structures strongly depend on the source and conditions during extraction and purification (Falshaw et al. 2001). Overall, the polymer chains comprise alternating (1→3)-linked β-D-galactopyranosyl and (1→4)-linked α-D-galactopyranosyl units. Some of the (1→3)-linked units occur as the 2- and 4-sulfates, whereas the (1→4)-linked units occur as the 2- and 6-sulfates, the 2,6-disufates, the 3,6-anhydride, and the 3,6-andydride-2-sulfate (Perceval 1972). Carrageenans are anionic polyelectrolytes. The half-ester content varies from 15% to 40%. Principally, there is a possibility of a continuous spectrum of carrageenan types including the biological precursors, which are modified by processing. After extraction and isolation, only the three types κ- (kappa), ι- (iota), and λ- (lambda) carrageenan are commercially available. They approach the

respective ideal type in chemical composition (Guiseley et al. 1980). The idealized repeating units of the three limiting types are shown in Fig. 3.11. Deviating from the idealized structures, the practical sulfate group content/dimer repeating unit is 1.03 rather than 1.0 for κ, 1.49 rather than 2.0 for ι, and 2.09 rather than 3.0 for λ (Chaplin 2007).

Several analyses have shown that carrageenans are highly polydisperse with typical number average molar masses in the range of 10^5–2×10^5 g/mol and typical weight average molar masses in the range of 3×10^5–6×10^5 g/mol (Piculell 1995).

Physico-chemical Characteristics of Carrageenans. Some selected properties of carrageenans are summarized in Table 3.3. Due to the variation in their chemical structure, carrageenans exhibit a wide spectrum of the rheological behavior (Mangione et al. 2003). Dependent on the type, they can form viscous solutions and also thermally reversible gels with a texture varying from soft and elastic to firm

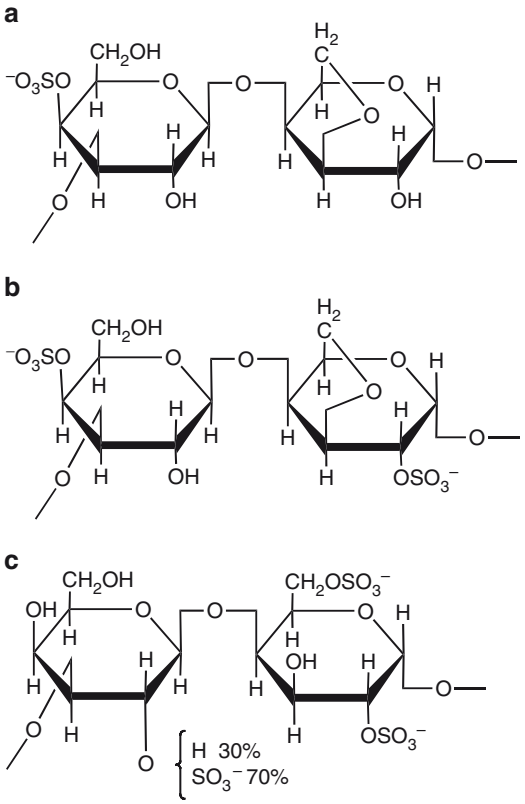

Fig. 3.11 Repeating dimer units of limit carrageenans. (**a**) κ-carrageenan: (1→3)-β-D-galactopyranose-4-sulfate-(1→4)-3,6-anhydro-α-D-galactopyranose-(1→3), (**b**) ι-carrageenan: (1→3)-β-D-galactopyranose-4-sulfate-(1→4)-3,6-anhydro-α-D-galactopyranose-2-sulfate-(1→3), (**c**) λ-carrageenan: (1→3)-β-D-galactopyranose-2-sulfate-(1→4)-α-D-galactopyranose-2,6-disulfate-(1→3)

Table 3.3 Selected properties of carrageenans (Davidson 1980; Imeson 2007)

	Carrageenan type		
Property	Kappa	Iota	Lambda
Solubility in hot water	T > 70°C	T > 70°C	Soluble
Solubility in cold water	Na-salt soluble; from limited to high swelling of K-, Ca-, and ammonium salts	Na-salts soluble, Ca-salts give thixotropic dispersions	All salts soluble; viscous pseudoplastic solutions
Gel formation	Thermo-reversible gels on cooling in the presence of appropriate counterions		Non-gelling
Gelation	Strongest with K^+	Strongest with Ca^{2+}	
Gel type	Brittle with syneresis; poor freeze-thaw stability	Elastic, no syneresis; good freeze-thaw stability	
pH stability	Stable at neutral alkaline pH; pH = 3.5: hydrolysis of polymer solutions but gels are stable		Hydrolysis below pH 4.3
Salt tolerance	Poor	Good	Good

and brittle as specified for the three types in Table 3.3. κ- and ι-carrageenans have the ability to form elastic gels in the presence of certain cations such as K^+ and Ca^{2+}. The molecular mechanism for the conformal transitions in the solution that result in the aggregation and gelation is still not completely understood. Comprehensive NMR studies have contributed to some progress.

Synergistic effects are obtained when combining carrageenans with other gum types. Brittle κ-carrageenan gels may be softened with, for example, locust bean gum. ι-Carrageenan has less specific ionic binding but the increased ionic strength allows helices to form junction zones in soft elastic gels with good freeze-thaw stability. λ-Carrageenan is non-gelling but is the type with the highest anionic charge density, which causes the best solubility, extended chain conformation, and strong electrostatic interaction in solution (Janaswamy and Chandrasekaran 2002; Kara et al. 2006).

Origin and Isolation of Carrageenans. Carrageenans are prepared from red seaweed (*Rhodophycae*). Different seaweeds produce different carrageenans, for example, *Chondrus crispus* (κ and λ), *Eucheuma cottonii* (κ), *Eucheuma spinosum* (ι), *Gigartina* (κ and λ), *Furcellaria* (κ and λ), by extraction and subsequent treatment/modification of the biological precursors μ- and ν-carrageenan. Seaweed selection, processing, and blending of different extracts can control the variations of the carrageenan types (Piculell 1995, 2006; Imeson 2007).

Alginate

Chemical Description of Alginate. (CAS 9005-38-3 Na) Alginate (Draget 2000; Cottrell and Kovacs 1980b; Moe et al. 1995; Draget et al. 2006) is a family of linear anionic polysaccharides, which can be considered as copolymers of (1→4) linked

α-L-guluronic acid (G) and β-D-mannuronic acid (M) residues. The linear chains are composed of homopolymeric regions of G- and M-blocks interspaced with regions of mixed sequences, MG-blocks (Grasdalen et al. 1979). Figure 3.12 shows a part of a sodium alginate chain. Depending on the seaweed extract, the isolation process, or the biotechnological procedure, the proportion and sequential arrangement of the two structural units vary widely. M and G blocks of various lengths can be present in the polymer chain. Consequently, for the description of the sequential structure not only the monomer composition (monad frequency) but also the diad and triad frequencies have to be known. The four diad (nearest neighbor) frequencies (F_{GG}, F_{GM}, F_{MG}, F_{MM}) and the eight possible triad frequencies (F_{GGG}, F_{GGM}, F_{MGG}, F_{MGM}, F_{MMM}, F_{MMG}, F_{GMM}, F_{GMG}) can be analyzed by NMR techniques (Grasdalen et al. 1979). The weight average molar mass of commercial sodium alginates varies from 4×10^4 to 5×10^5 g/mol. But some alginates with molar masses higher than 10^6 g/mol have also been isolated.

Physico-chemical Characteristics of Alginate. Alginate composition, structure, and molar mass govern the functional properties. The solubility of alginate in water is related to the rate of dissociation and the type of the counterion. At pH < 3, both the M- and G-structures will precipitate as alginic acid. However, alternating structures precipitate at lower pH values compared to the alginates containing more homogeneous block structures. Neutralization of the alginic acid occurs at pH > 4, where it is converted into its corresponding salt. Sodium alginate is an example of a water-soluble alginate.

The intramolecular electrostatic repulsion between the neighboring negative charges of each monomer unit forces alginate molecules into an extended random coil conformation (Smidsrød and Hang 1968). This results in highly viscous solutions even at relatively low alginate concentration. The dynamic viscosity increases exponentially with the molar mass, while the intrinsic flexibility of the alginate chains in solution increases in the order GG < MM < MG (Smidsrød et al. 1973). On the other hand, the selectivity for cation binding and gel forming properties strongly depend on the composition and sequence. Divalent cations preferably bind to the G-blocks. The ability to form ionotropic gels is based on this selective binding of cations. Gel-like networks are also formed with the polycation chitosan. As typical for linear homogeneously charged polyelectrolytes,

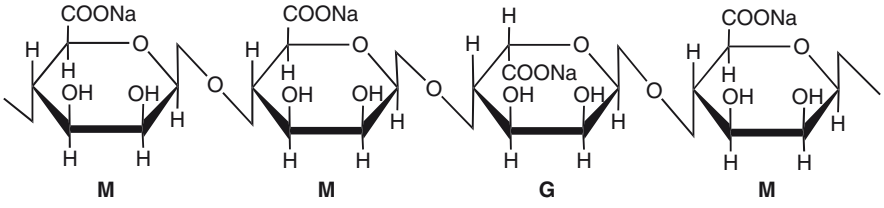

Fig. 3.12 Principal chemical structural units of a sodium alginate polymer chain

the chain conformation and, therefore, the solution viscosity strongly depend on the ionic strength.

The rheological behavior of sodium alginate solutions depends on the concentration and the shear rate. Higher concentrated solutions exhibit pseudoplastic flow even at low shear rates. At lower concentrations, the Newtonian behavior is observed at low shear rate whereas the solutions become pseudoplastic at higher shear rate (Draget 2000).

Alginate as a dry powder and, in particular as a solution, is subject to degradation leading to rapid decrease of the chain length detectable by decreasing viscosity. Many microorganisms digest alginate. In a deep freezer, sodium alginate may be kept for several years without significant degradation.

Origin and Isolation of Alginate. Alginates are quite abundant in nature. Commercial sodium alginates are generally produced from marine brown algae, though they may also be synthesized as an exocellular material by some bacteria (Chapman 1980). Moreover, biosynthesis is possible yielding alginates over a very wide range of tailored composition (Valla et al. 1996).

3.2.1.5 Microbial and Animal Polysaccharides

Polysaccharides produced biotechnologically by bacteria are biopolymers with novel and partially unique functional properties. Examples, which are interesting for food applications are xanthan, gellan, and curdlan, though the WHO has at the present time certified the latter only for a few countries.

Xanthan

Chemical Description of Xanthan. (CAS# 11138-66-2) Xanthan is a high molar mass anionic polyelectrolyte for which the principal chemical structure is shown in Fig. 3.13. It occurs as a mixed salt of sodium, potassium, and calcium. Its backbone consists of β-(1→4)-D-glucopyranosyl units with every second unit having a trisaccharide side chain attached at the C-3 position, one D-glucuronosyl unit between two D-mannosyl units. Therefore, xanthan may also be considered as consisting structurally of pentamers. Approximately, 40–50% of the terminal mannosyl units are 4,6-pyruvated. The non-terminal mannosyl units are mostly 6-acetylated.

The molar masses reported in the literature vary from 1.5×10^5 g/mol to several million, but are probably in the order of two million. Association phenomena observed for xanthan gum could explain these variations (Sworn 2000b; Morris 1995, 2006; Cottrell et al. 1980; Elias 1992). However, a consensus of the opinion exists that the polydispersity is relatively low.

Physico-chemical Characteristics of Xanthan. Xanthan is soluble in cold water. It hydrates rapidly in cold water without lumping if properly dispersed into the solvent. It is considered to be mainly non-gelling. The solutions show a very pronounced pseudoplastic behavior. The viscosity progressively reduces with increasing

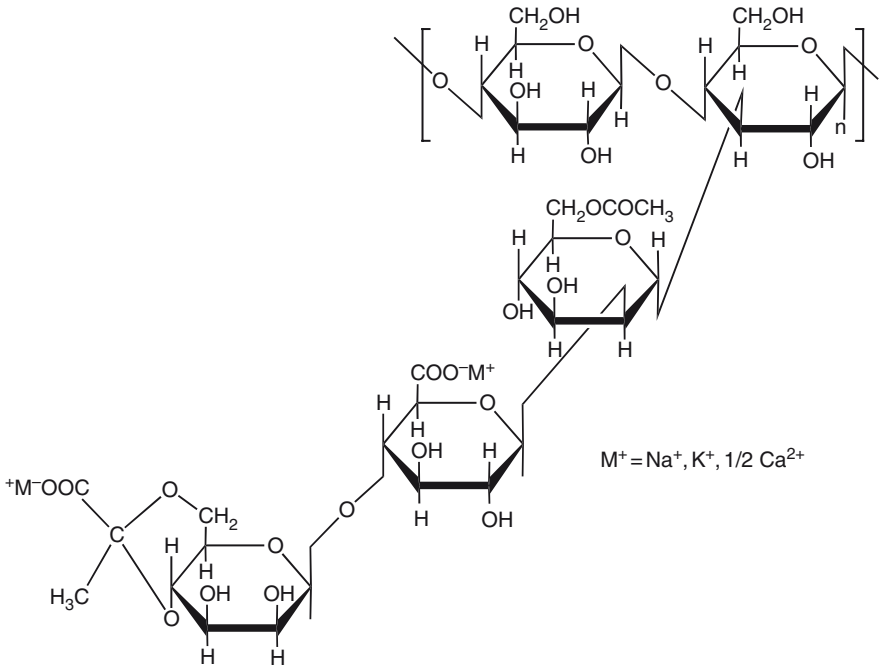

Fig. 3.13 Principal chemical structure of xanthan gum

shear stress but instantaneously recovers after removal of the shear stress, subsequently returning to the initial viscosity. In general, the solution viscosity has been found to be stable over a wide range of pH (2–12) and temperature. The high viscosity is assigned to the network formation due to the H-bonding and polymer chain entanglement. Two chains may be aligned to form a double helix, giving a rather rigid rod configuration. The conversion between the ordered double helical conformation and the single more-flexible extended chain may take place over hours between 40°C and 80°C. The shielding of the backbone by side chains could explain the extraordinary resistance to enzymatic degradation. Xanthan undergoes cryogelation (Giannouli and Morris 2003).

Contrary to the typical polyelectrolyte behavior, the addition of salt to a hitherto salt-free xanthan solution causes the viscosity to increase when the xanthan concentration is higher than 0.15%. An increase of viscosity has also been observed when heating salt-free solutions, but with salt (0.1% NaCl) only minor variation of the viscosity is observed in the temperature range 10–90°C (Cottrell et al. 1980a).

Synergistic interaction with guar gum leads to an enhanced viscosity, whereas with LBG and konjac mannan soft, elastic thermo-reversible gels are obtained at higher concentration (Sworn 2000b).

Origin and Isolation of Xanthan. The *Xanthomonas campestris* bacterium produces the xanthan gum in a pure culture of the bacterium by an aerobic fermentation process in a glucose medium. Use of different strains or fermentation conditions

may give rise to differing degrees of actelylation and pyruvylation. Xanthan may contain cellulases, which prevents its use with cellulose derivatives.

Gellan

Chemical Description of Gellan. (CAS# 71010-52-1) Gellan (Sworn 2000a) is a high molar mass anionic polyelectrolyte. The principal chemical structure in Fig. 3.14 shows the tetrasaccharide repeating unit composed of one rhamnose, one glucuronic acid, and two glucose units. The 3-linked glucose unit is substituted with glyceryl at O(2) and with acetyl at O(6). It can, therefore, be designated as →4)-L-rhamnopyranosyl-α-(1→3)-D-glucopyranosyl-β-(1→4)-D-glucuronopyranosyl-β-(1→4)-D-glucopyranosyl-β-(1→ (Chaplin 2007). Molar masses are in the range up to 5×10^5 g/mol. The degree of esterification depends on the production process. Low acyl (deacetylated) and high acyl specifications are commercially available.

Physico-chemical Characteristics of Gellan. The solubility and solution properties depend on the degree of substitution and the type and concentration of ions present in the solution. Low acyl gellan is much more sensitive to ions and frequently a sequestrant has to be added for hydration, which generally takes place at temperatures above 90°C. The hydration of high acyl gellan gum is less dependent on the concentration of ions. Heating to 85–95°C is in general sufficient to fully hydrate the gum. Gellan is able to withstand heating to 120°C. The viscosity increases with the degree of acetylation. A gellan solution may invisibly hold particles in suspension but, unlike other gelling agents, without significantly increasing the solution's viscosity.

Thermo-reversible gelation takes place upon cooling of solutions in the presence of gelling cations in the case of low acyl and without gelling cations in the case of high acyl. The resulting gel texture depends on the degree of acetylation and can cover a wide range. Low acyl types form hard, non-elastic brittle gels, whereas high acyl types yield soft, elastic, transparent, and flexible gels. Comparison with other gelling agents manifests this wide range (Fig. 3.15). Nevertheless, the exact texture and quality of the gel is influenced by the concentration of divalent cations present.

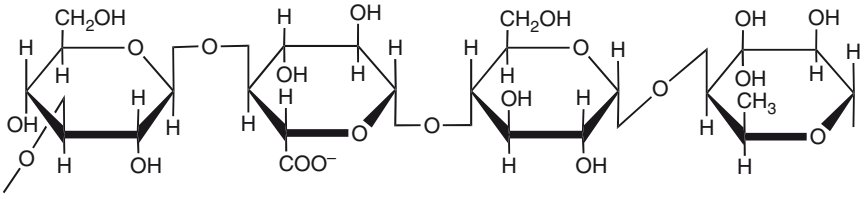

Fig. 3.14 Principal chemical structure of gellan gum

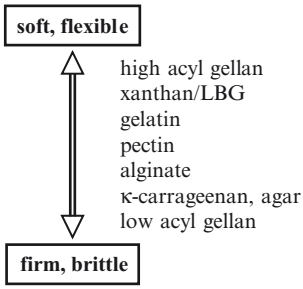

Fig. 3.15 Gel texture of different gelling macromolecular materials demonstrating the wide range of gel texture for gellan gum

Origin and Isolation of Gellan. Gellan is prepared commercially by aerobic submerged fermentation from the microorganism *Sphingomonas elodea* (Chandrasekaran and Radha 1995). High and low acyl types are available as off-white powders differing in their degree of decetylation. The latter is obtained by alkali treatment prior to isolation.

Dextran

Chemical Description of Dextran. Dextrans (CAS# 9004-54-0) are mainly linear neutral polymers of α-D-glucose linked by α-(1→6) glycosidic bonds, which can have variable amounts of α-(1→3) branches. Partially, the links in the main chain can be α-(1→4) or α-(1→2) links instead of α-(1→6) links. The fermentation process governs the chain architecture, molar mass, and polydispersity. The number - average of the molar mass of native dextrans is in the range of 2×10^5 g/mol. Due to the strong tendency to associate in the aqueous solution, apparent molar masses up to 5×10^8 have been obtained (Elias 1992).

Physico-chemical Characteristics of Dextran. Overall, dextrans are well soluble in water. Non-soluble portions result from higher degree of branching.

Origin and Isolation of Dextran. Microbial fermentation processes of sucrose yield dextrans, which are commercially supplied as powders or solutions. The bacteria used determine the chain architecture.

Chitosan

Chemical Description of Chitosan. (CAS# 9012-76-4) Chitosan (Winterowd and Sandford 1995; Vårum and SmidsrØd 2006) is a linear polysaccharide, which can be considered as a copolymer consisting of randomly distributed β(1→4) linked D-glucosamine and N-acetyl-D-glucosamine as illustrated in Fig. 3.16; block arrangement has also been reported (Inoue 1997). The composition is indicated by the degree of acetylation (DA), the fraction of acetyl-glucosamine units. The

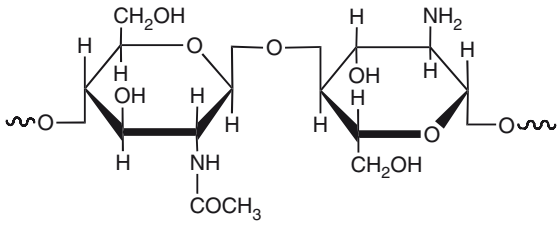

Fig. 3.16 Principal chemical structure of chitosan, deacetylated (*right*) and acetylated (*left*) chain units

molar mass depends on the source and the isolation technology, but it can reach values of about 5×10^5 g/mol. Lower molar masses and oligomers are obtained by the chain degradation under various conditions frequently yielding products, which differ from the composition and sequence arrangement of the parent molecules (Terbojevich 2000).

Physico-chemical Characteristics of Chitosan. Chitosan can be classified as a non-permanently charged cationic polyelectrolyte. Due to a pK_a value of approximately 6.5, chitosan is positively charged and soluble in acidic to neutral medium. The charge density and solubility depend on the DA. Only chitosan with a DA not exceeding 40% is soluble in acidic aqueous medium. Exceptions are oligomers, which have a higher solubility across a broader pH range. Chitosan forms gels with tripolyphosphate and alginate. Moreover, it has a very good film-forming ability (Domard and Domard 2002).

Origin and Isolation of Chitosan. Chitin, the main source of chitosan, has been evaluated to be as abundant as cellulose with an annual production of 10^{10}–10^{12} tons in biomass (Roberts 1992). Chitosan itself is much less present in nature. It has only been observed in some microorganisms and certain fungi. Only very recently, the commercial isolation from fungi has started. The main process of the alkaline deacetylation of crustacean chitins remains.

3.2.2 Proteins

Proteins are natural macromolecules composed of linear chains of amino acids. The possible sequences and frequency of 20 existing amino acids, more precisely 19 amino acids and one imino acid, in the chain give rise to their enormous variety. Proteins have a central role in all living organisms with a wide range of functions. Large amounts of proteins are directly used as food. The potential use for non-traditional applications is in the process of being extended.

3.2.2.1 Gluten

Chemical Description of Gluten. (CAS# 8002-80-0) Gluten is a complex mixture of gliadins (monomeric gluten proteins) with molar masses in the range of 3×10^4–8×10^4 g/mol (MacRitchie et al. 1990) and glutenins (polymeric gluten proteins) with molar masses in the range of 8×10^4 g/mol to several million (Kasarda 1989). Gliadins and glutenins comprise about 80% of the proteins contained in wheat seed. Both have unusually high levels of proline and glutamine and are therefore designated as "prolamins" (Shewry et al. 1986).

Gliadins represent a highly heterogeneous mixture of monomeric gluten proteins. Three structurally distinct groups, α-, γ-, and ω-types, can be distinguished (Shewry et al. 1986). The α- and γ-types are classified as sulfur-rich prolamins, whereas the ω-type gliandins are classified as sulfur-poor prolamins.

Wheat glutenin is a heterogeneous mixture of disulfide stabilized polymers of high-molar-mass glutenin subunits (HMM-GS) and low-molar-mass glutenin subunits (LMM-GS). More than 20 different HMM-GS have been identified so far in wheat varieties and new ones are being discovered frequently (Veraverbeke and Delcour 2002). Although LMM-GS show strong similarities with α- and γ-type gliadins, commonly classified as sulfur-rich prolamins, they differ in one very important characteristic: apart from intra-chain disulfide bonds, inter-chain disulfide bonds that lead to incorporation of LMM-GS in glutenin polymers also occur in LMM-GS. In these polymers, they form covalent links with the HMM-GS that form a separate third class of prolamins, the high-molar-mass prolamins, which typically have a higher content of glycine than the other two classes of prolamins (Shewry et al. 1986; Veraverbeke and Delcour 2002). Estimations of the size and structure of glutenin subunits and polymers are highly troubled by their low solubility in conventional buffers and the lack of crystallinity (Bottomley et al. 1982). Despite progress in unraveling the complexity, the structure is still largely a matter of speculation (Veraverbeke and Delcour 2002).

Physico-chemical Characteristics of Gluten. Glutenins show very low solubility in water due to a low content of amino acids with ionizable groups, the high content of non-polar amino acids and glutamine, and their high molar mass (Singh and MacRitchie 2001). Gliadins are soluble in distilled water but aggregate in salt solution (Van Vliet et al. 2002).

Surprisingly, few studies have been performed concerning the interfacial behavior of the wheat components (Örnebro et al. 2000). From studying the behavior of adsorbed layers of the four major wheat protein fractions at the air–water interface it was concluded that surface pressure increases in the order albumins < globulins < glutenins < gliadins (Keller et al. 1997). Further, a higher ability of gliadins to reduce the surface tension compared to glutenins has been found (Eliasson and Larsson 1993; Balla et al. 1997). Sprinkling the gluten powder on the water surface revealed that the film was almost completely elastic (Kokelaar et al. 1991).

Origin and Isolation of Gluten. Gliadin and glutenin exist, conjoined with starch, in the endosperm of some grass-related grains, notably wheat, rye, and barley. Being insoluble in water, they can be purified by washing away the associated starch.

Gluten proteins are strongly associated with baked products. However, the unique properties of wheat proteins have stimulated an interest in their use for other applications than traditional ones (Örnebro et al. 2000).

3.2.2.2 Milk Proteins

Bovine milk contains, in addition to water, lactose, fat, and other minor components, about 3.0–3.6 wt% proteins. Of this, caseins and whey proteins are the two major fractions. Detailed description of the milk proteins is presented in several reviews and book chapters (Ennis and Mulvihill 2000; Fox 1989; Fox 1992; Holt 1992; Creamer and MacGibbon 1996).

Caseins

Chemical Description of Caseins. Caseins (from Latin caseus "cheese") (CAS# 9000-71-9) are the most predominant phosphoproteins found in milk. The four principal primary proteins of the highly heterogeneous casein fraction are summarized in Table 3.4. Caseins can vary in their net charge, hydrophilicity, and metal binding. In milk they are present in the form of large approximately spherical micelles (molar mass about 10^8 g/mol), which can be separated from the molecularly dispersed whey proteins by ultracentrifugation.

Physico-chemical Characteristics of Caseins. Caseins are extremely heat-stable proteins. They do not coagulate by heat. They are insoluble at their isoelectric point, at about pH 4.6. However, the solubility behavior varies for casein fractions isolated from milk. Acid caseins are insoluble in the pH range 4–5, but they become soluble if the pH is increased above 5.5. Solutions of 10–15 wt% having high viscosity can be prepared at pH 6–7. They are also soluble at pH < 3.5, but here the solutions are more viscous and become even gel-like. Rennet caseins are insoluble at pH 7 but soluble at pH exceeding 9. Calcium caseinate is the only milk protein

Table 3.4 Casein fractions and some characteristics typical for bovine milk (Ennis and Mulvihill 2000)

	Caseins			
Parameter	α_{s1}-casein	α_{s2}-casein	β-casein	κ-casein
Concentration wt%	0.9–1.5	0.3–0.4	0.9–1.1	0.3–0.4
Isoionic pH	4.94	5.45–5.23	5.14	5.61
Molar mass ($\times 10^{-4}$ g/mol)	2.36	2.52–2.54	2.4	1.9

system reported to exhibit reversible thermal gelation. Overall, milk proteins have good surface active properties ranked in the order β-casein > monodispersed casein micelles > serum albumin > α-lactalbumin > α_s-casein = κ-casein > β-lactoglobulin. Surface films of sodium caseinate or β-casein have the best flexibility and lowest viscoelasticity compared with the films of other materials. Caseins are good fat emulsifiers. The water solubility of films formed from caseins/caseinates depends on the pH conditions used in their preparation. The water vapor permeability of the films depends on the protein type.

Origin and Isolation of Caseins. Caseins are generally manufactured from the skim milk by destabilizing the micelles. Numerous processes are known. The main products obtained are mineral acid casein, lactic acid casein, and rennet casein. Fractionation is possible and other caseinates may be obtained by different manufacturing processes. Spray-dried sodium caseinate is the most commonly used water-soluble caseinate.

Whey Proteins

Chemical Description of Whey Proteins. Whey is a by-product of cheese or casein production and has several commercial uses. Whey proteins primarily include α-lactalbumin, β-lactoglobulin, immunoglobulins, and serum albumin but also numerous minor proteins. The four principal proteins of the highly heterogeneous whey protein fraction are summarized in Table 3.5. α-Lactalbumin is a calcium metalloprotein with four intramolecular disulfide cross-links, for which genetic variants exist. β-Lactoglobulin has two intramolecular disulfide cross-links and one free SH group. Many genetic variants are known which vary in their degree of glycosylation.

Physico-chemical Characteristics of Whey Proteins. Whey proteins are globular proteins (Chen et al. 2006), soluble in their native forms in the ionic environment of milk, almost independent of pH. But they become insoluble at their isoelectric point (pH about 5) at very low ionic strength. In contrast to caseins, whey proteins

Table 3.5 Whey protein fractions and some characteristics typical for bovine milk (Ennis and Mulvihill 2000)

	Whey proteins			
Parameter	α-lactalbumin	β-lactoglobulin	Immunoglobulins	Serum albumin
Concentration (wt%)	0.07–0.15	0.2–0.4	0.06–0.1	0.01–0.04
Isoionic point	4.2–4.5	5.2		5.3
Molar mass ($\times 10^{-4}$ g/mol)	1.4	1.8	15-90	6.6

denature at temperatures above 70°C and become insoluble. Then they form thermally irreversible gels of different quality. Solutions of non-denatured whey proteins are much less viscous than caseinate solutions. They exhibit Newtonian flow at concentrations in the range of 4–12 wt% but become pseudoplastic in the range of 18–29 wt% concentration. As already mentioned for caseins, milk proteins exhibit good surface-active properties. Films, formed when thermally induced disulfide cross-linking takes place, are excellent gas barriers (Madene et al. 2006), while the incorporation of lipids reduces the water vapor permeability. Tensile strengths were found to be similar to synthetic films. The films were generally flavorless, and transparent to translucent depending on the protein source (Chen 1995; Lee and Rosenberg 2000).

Cold induced gelation of globular whey protein (Barbut and Foegeding 1993; Chen et al. 2006) can be achieved by adding calcium to a preheated mixture. A mechanism of cross-linking carboxyl groups with calcium has been suggested for the gelation of prenaturated whey proteins at ambient temperature (Roff and Foegeding 1996; Chen et al. 2006).

Because of their flexibility and amphiphilic nature, globular proteins rapidly adsorb on the emulsion interface, where they self-aggregate and form continuous and homogeneous membranes around oil droplets through intermolecular beta-sheet interactions (Lefèvre and Subirade 2003; Chen et al. 2006). By coating oil droplets with charged layers, protein films provide an electrostatic barrier against flocculation and coalescence.

Various procedures can yield microcapsules from whey proteins (Rosenberg and Lee 2004).

Origin and Isolation of Whey Proteins. Whey, the source of whey proteins, remains after removal of fat and caseins from milk. The following products are isolated: whey powders of different quality (demineralized, delactosed, and demineralized-delactosed), whey protein concentrate (WPC), whey protein isolate (WPI), lactalbumin, and individual whey protein fractions. WPC contains a low level of fat and typically 35–80 wt% protein. During the isolation of WPI, the removal of fat and lactose is intended. The protein content becomes >90 wt%. β-Lactoglobulin is the most important whey protein (Madene et al. 2006).

It is likely that the range of proteins recovered from milk will extend in the future. Tailoring of milk protein products to meet specific functional requirements for individual applications will become increasingly important. The use of milk protein products in emerging technologies, such as the manufacture of edible films (Chen 1995) and the microencapsulation of ingredients (Rosenberg and Yong 1993) will benefit from further development (Ennis and Mulvihill 2000).

3.2.2.3 Gelatin

Chemical Description of Gelatin. (CAS# 9000-70-8) Gelatins (Ledward 2000) vary widely in their size and charge distribution. However, they generally have a characteristic primary structure determined by the parent collagen. Almost every third unit in

all chains is glycine, followed by proline and 4-hydroxyproline as next frequently occurring residues. A typical amino acid composition of type A gelatin derived from pigskin is (residues per 100 units): glycine 33, prolin 13, alanine 11, hydroxyproline 9, arginine 5, serine 3.5, aspartic acid 3, lysine 3, glutamic acid 2.5, and further leucine, valine, phenylalanine, threonine, isoleucin, hydroxylysine, methionine, histidine, and tyrosine. Especially the minor components can vary, depending on the source of the raw material and processing technique. In type B gelatins, aspargine and glutamine are missing due to their conversion into aspartic acid and glutamic acid (Ledward 2000).

Gelatin is a heterogeneous mixture of single- or multi-stranded polypeptides, each with extended left-handed proline helix conformations and containing between 300 and 4,000 amino acids (Chaplin 2007).

Commercial gelatins are highly heterogeneous in size. Individual molecules may be single chains of molar masses less than 5×10^4 g/mol or multi-strand polymers with molar masses of over one million. The gelatin molecules are subdivided into several molar mass ranges corresponding to the most commonly occurring sizes, with the highest molar mass range covering 3.4×10^5–5.4×10^5 g/mol and the lowest one covering 1×10^4–2.5×10^4 g/mol. Nevertheless, each of these fractions is also heterogeneous with regard to the size and shape (Ledward 2000).

Physico-chemical Characteristics of Gelatin. Gelatins in their pure form are translucent, brittle solid substances, which are colorless or slightly yellow, almost tasteless, and odorless. Gelatins melt when heated and solidify when cooled again. Mammalian gelatins dissolve in hot water forming solutions of high viscosity, which gel on cooling below 35–40°C. Alternatively, the fish skin gelatin has a lower gelation temperature, typically around 5°C for cold-water fish skin gelatin. However, a gelation temperature of about 12°C was reported for warm-water fish skin gelatin (Avena-Bustillos et al. 2006). Gelatin is also soluble in most polar solvents. The aqueous solutions show viscoelastic flow and streaming birefringence. The solubility of the gelatin is determined by the source and the method of manufacture. If gelatins are put into contact with cold water, only portions dissolve, however, they can take up water up to 5–10 times its own weight while swelling to an elastic mass.

Gelatins are amphiphilic and can behave as polyelectrolytes in aqueous solution, depending on the pH. The isoelectric points of type A gelatins are in the range of pH 7–9.4, whilst type B gelatins have isoelectric points in the range of pH 4.8–5.5. Apart from these differences, type A gelatins usually have lower intrinsic viscosities for a given molar mass than type B gelatins. The amphiphilic nature provides good emulsifying property.

Gelatin gels formed on cooling of solutions with concentrations above about 1 wt%, depending on the quality of the gelatin and the pH, are clear, elastic, transparent, and thermo-reversible. On warming to 35–40°C, the gels will dissolve again. Whereas from dilute solutions gels with a “melt in mouth” texture are obtained, the gels from higher concentrated solutions exhibit elastic gum-like textures. Gelatin gels from aqueous solutions exist over only a limited temperature range, the upper limit being the melting point of the gel, which depends on the gelatin

grade and concentration, and the lower limit, the ice point at which ice crystallizes (Ledward 1986).

In solution, gelatins undergo a coil-helix transition followed by the aggregation of helices to form collagen-like right-handed triple-helical proline/hydroxyproline rich junction zones. Gelatin films with higher triple-helix content swell less in water and are therefore much stronger (Bigi et al. 2004; Chaplin 2007).

The amphotheric hydrocolloid gelatin forms complex coacervates with anionic polysaccharides such as gum arabic. At low pH, gelatin becomes positively charged and also forms coacervates with negatively charged gellan gum (Madene et al. 2006).

Fish skin gelatins (Avena-Bustillos et al. 2006) of low pyrolidine content are far poorer gelling agents than gelatins of similar molar mass derived from warm-blood mammals (Ledward 2000). Nevertheless, the low water vapor permeability observed for warm-water fish gelatin, and particularly for cold-water fish gelatin films (Avena-Bustillos et al. 2006), can be advantageous for encapsulation applications to reduce water loss at low temperatures such as in refrigerated or frozen food systems.

Origin and Isolation of Gelatin. Gelatins do not occur naturally but are manufactured from collagens by processes that destroy the secondary and higher structures of collagen. The latter is the major constituent of all white fibrous connective tissue occurring in animals (cartilage, sinews, skin, ossein). The process of manufacture is very complex using hides, skins, or bones from domesticated cattle, pigs, and horses as preferred sources, but also fish skin is used as a source. Two principal processes are distinguished finally yielding two principally different types of gelatin: type A gelatins by acid treatment (pH 1.5–3.0) and type B by alkaline treatment (pH 12) of collagen. Overall, the source and the process determine the final gelatin properties. Numerous commercial gelatin types are available in the market.

3.2.3 Lipids

Characteristic for lipids is their general insolubility in water; they are hydrophobic. Lipids involve molecules and substances of large diversity and structural variety such as oils, fats, waxes, and phospholipids. These are widely distributed in nature.

3.2.3.1 Fatty Acids and Fatty Alcohols

Chemical Description of Fatty Acids and Fatty Alcohols. Two subgroups of fatty acids may be distinguished, saturated and unsaturated acids, which in addition can be of variable length. Saturated fatty acids are linear monocarboxylic acids of the overall formula $CH_3(CH_2)_nCOOH$. Alternatively, unsaturated fatty acids have one or more double bonds in their chain, giving rise to different chain configurations, namely cis and trans. Further, short-, medium-, and long-chain fatty acids are dis-

tinguished, which differ in the number of carbons in the aliphatic tail, having less than 8, 8–14, and more than 16 carbons, respectively. In fatty alcohols, a hydroxyl group has replaced the carboxylic group.

Physico-chemical Characteristics of Fatty Acids and Fatty Alcohols. Short chain aliphatic acids are miscible in water; however, the water-solubility rapidly decreases with increasing chain length. The melting points of fatty acids vary over a wide range, with the unsaturated acids having a much higher melting point. Examples are (Beyer 1968): palmitic acid ($n=14$) 62.6°C, stearic acid ($n=16$) 69.4°C, behenic acid ($n=20$) 74–78°C. At room temperature, fatty acids tend to undergo auto-oxydation.

Fatty alcohols behave as non-ionic surfactants and have emulsifying properties.

Origin and Isolation of Fatty Acids and Fatty Alcohols. Fatty acids are produced by the hydrolysis of the ester linkage of naturally occurring fats and oils, which are in general triglycerides. Glycerol is obtained as the byproduct from this process. Reduction of fatty acids yields fatty alcohols.

3.2.3.2 Glycerides

Chemical Description of Glycerides. Triglyceride (triacylglycerol, triacylglyceride), diglyceride (diacylglycerol), and monoglyceride (monoacylglycerol) belong to the family of glycerides. The principal chemical structures are shown in Fig. 3.17. Three, two, or only one fatty acid chains are covalently bonded to a glycerol molecule by ester linkages. In triglyceride, the three fatty acids may be the same, and may differ by one or all three. Thereof, the acids may be saturated or unsaturated. The most common residues are those with 16, 18, and 20 carbons. The same holds for diglycerides. Here, the two fatty acids can be located at any one of the three carbon positions. In monoglyceride, the fatty acid can be located either at the C-1 or C-2 position.

Physico-chemical Characteristics of Glycerides. Glycerides are not soluble in water. Di- and monoglycerides have emulsifying properties. The melting points of the glycerides strongly depend on the chemical nature but also on the symmetry of the fatty acid residues, their distribution over the carbon positions. For example, the highest melting point of milk fats has the fully symmetric tristearate with $T_m = 72°C$ (Walstra 1999).

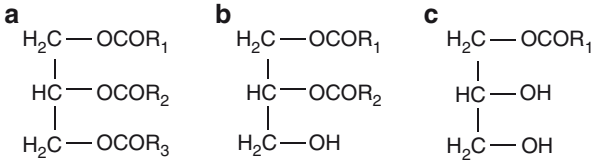

Fig. 3.17 Glycerides. (**a**) triglyceride, (**b**) diglyceride, (**c**) monoglyceride

Origin and Isolation of Glycerides. Triglyceride is the main constituent in animal fats and plant/vegetable oils. Most natural fats contain a mixture of different triglycerides. The heterogeneity of the mixture determines the span of the melting range. The commercial source of mono- and diglycerides is the same as for triglycerides, but total synthesis is also possible.

3.2.3.3 Waxes – Beeswax, Carnauba Wax, Candellia Wax

Chemical Description of Waxes (Parish et al. 2002). Waxes are esters of fatty acids. In contrast to fats and oils, the fatty acids are not esters of glycerol but of higher primary monovalent alcohols. The main components of beeswax (CAS# 8012-89-3) are triacontylpalmitate (about 75%), triacontylcerotinate (about 10%), and paraffin (about 15%) (Beyer 1968).

Physico-chemical Characteristics of Waxes. Waxes are practically insoluble in water. The color of beeswax varies from nearly white to brownish. It melts in the range of 62–64°C. Beeswax (Ross Waxes 2008a) is compatible with most other waxes and oils, fatty acids, glycerides, and hydrocarbons.

Carnauba wax (CAS# 8015-86-9) (Ross Waxes 2008b; Strahl and Pitsch 2008a) is one of the hardest natural waxes. The melting point is in the range 78–85°C (typically 83°C). The compatibility with other materials is similar as for beeswax.

Candelilla wax (CAS# 8006-44-8) (Ross Waxes 2008c; Strahl and Pitsch 2008b) is soluble in many organic solvents. It is light brown to light yellow, and melts in the range of 67–79°C. It is not as hard as carnauba wax. It is compatible with all vegetable and animal waxes, fatty acids, a large variety of natural and synthetic resins, glycerides, and hydrocarbons in certain proportions,

Origin and Isolation of Waxes. Waxes are isolated from animal and plant products. Beeswax is secreted by young honey bees to construct the honeycomb. Carnauba wax is obtained from the leaves of palm trees preferably in Brazil. Candellila wax is derived from the leaves of the Candelilla shrub, which grows in the northern Mexico.

3.2.3.4 Phospholipids – Liposomes

Chemical Description of Phospholipids. The general chemical structure of one of the main phospholipids or phosphodiglycerides, i.e., phosphatidylcholine, is shown in Fig. 3.18. Phospholipids contain two long chain fatty acids. The third hydroxyl group of the basic glycerol is modified with the phosphoric acid linked to a base such as choline or ethanolamine. Depending on the position of the phosphor-containing group, it is linked to the primary or secondary hydroxyl group of the glycerin, α and β phospholipids are distinguished (Beyer 1968). As with triglycerides, numerous species are possible by variation of the different head groups and fatty acyl substitution at the first and second position of the glycerol backbone (Weiner 2002). The most

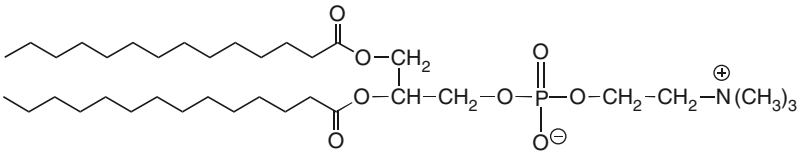

Fig. 3.18 Phospholipid – phosphatidylcholine

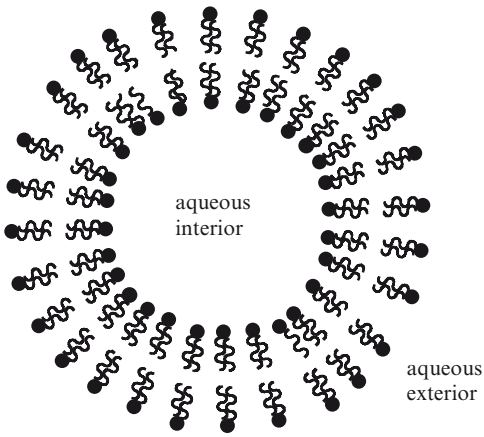

Fig. 3.19 Schematic structure of a liposome

abundant phospholipids are lecithins (phosphatidylcholine) (Taylor et al. 2005), where the base is choline. The fatty acid components may be saturated or unsaturated, for example palmitic, stearic, oleic, linoleic, or linolenic acid. Other polar lipids are kephalins (phosphatidyl-ethanolamines) where the base is ethanolamine.

It has to be mentioned that the name lecithin is also used for the naturally occurring mixture of glycolipids, triglycerides, and phospholipids.

Physico-chemical Characteristics of Phospholipids. Phospholipids are ionic amphiphiles (betains). Diacyl phospholipids generally form liquid crystalline suspensions as long as the temperature is held at or above the phase transition. Due to the amphiphilic character they function well as emulsifying and dispersing agents (Weiner 2002). When mixed with water, they aggregate or self-assemble into well organized and defined structures, and bilayers. Applying energy during the mixing process forces the bilayer to form liposomes, which in general do not form spontaneously (Taylor et al. 2005). In liposomes, an aqueous interior is separated by one or more phospholipid bilayers from the aqueous exterior (Fig. 3.19) (Lasic

1998). The manufacturing techniques used and the intensity of mixing employed, govern the size of the liposomes. The mesoscale shape taken by the liposome is a balance between applied mechanical forces and the tendency to assume specific self-assembled structures (Winterhalter and Lasis 1993). Generally, liposomes are only stable for a defined period of time; i.e., they are kinetically but not thermodynamically stable (Reineccius 1995).

One of the key parameters for liposomal systems is the so-called gel to liquid crystalline transition temperature, where the bilayer loses much of its ordered packing structure due to the "melting" of hydrocarbon chains of the lipids. Typically, longer chains, saturation of the acids, and strong head group interactions translate into higher phase transition temperatures. Liposomal content may leak out fast, especially around or above the gel to liquid crystalline temperature. In addition, liposomal properties and functionality depend on external parameters, such as pH and ionic strength of the medium (Taylor et al. 2005, see also Sect. 2.3.11).

Origin and Isolation of Phospholipids. Phospholipids are present in all animal and plant cells. Commercially, they are isolated from the egg yolk (lecithin, CAS# 93685-90-6) and soybean oil (lecithin, CAS# 8002-43-5) (Hsieh et al. 2002), but are also produced from milk fat globular membrane isolated from buttermilk (Thompson and Singh 2006). Lecithin is commercially available at high purity.

3.2.4 Others

3.2.4.1 Polyvinylpyrrolidone (PVP)

PVP, 1-Ethenyl-2-pyrrolidoinone homopolymer, (CAS# 9003-39-8), for which the chemical structure is shown in Fig. 3.20, is a synthetic neutral polymer with molar masses in the range of 10^4–5×10^5 g/mol. PVP powder is well soluble in water and organic solvents. The viscosity of the solution depends on the molar mass and the concentration. Aqueous solutions exhibit Newtonian behavior. The good film forming ability makes it an excellent polymer for coatings, which requires good temperature stability (Blecher et al. 1980).

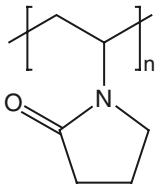

Fig. 3.20 Chemical structure of the polyvinylpyrrolidone

3.2.4.2 Paraffin

Paraffin (CAS# 8002-74-2) (Ross Waxes 2008d; Strahl and Pitsch 2008c) is a family of linear hydrocarbons with the general formula C_nH_{2n+2}. Dependent on the number of carbon atoms n, which can vary from 1 to about 40, they behave at ambient temperature as gas, liquid, or solid. Paraffin wax, the solid form, has $n > 20$. It is a white, odorless, tasteless waxy material, which is also available at food-grade quality. Paraffin is edible but not digestible. Melting points ranging from 48 to 95°C are reported by suppliers and in table books (INCHEM 2008). The source is petroleum but synthesis is also possible.

3.2.4.3 Shellac

Shellac (CAS# 9000-59-3) is secreted by the lac insect *Laccifer lacca (Kerria lacca)*, found in the forests of northeast India, Thailand, Bangladesh, Indochina, and China. The secretion is collected from trees and processed in several steps to form shellac, which is soluble in alkaline media (ammonia, sodium carbonate, sodium hydroxide) and in several organic solvents. The exact chemical composition of shellac is unknown. It appears to be composed of a network of hydroxy fatty acid esters and sesquiterpene acid esters with a molar mass of about 1,000 g/mol. The composition is a function of the source and time of harvest. The physical properties of shellac may also vary. For example, the reported melting point ranges from 77°C to 120°C. Shellac is soluble in ethanol, methanol, glycols, glycol ethers, and alkaline water (Yates and Field 1960). Coatings obtained from alcoholic solutions are of superior durability and hardness. It is edible.

India, Thailand, and China are the main producers. The production volume is difficult to estimate but is assumed to be of the order of 10,000–20,000 tonnes per year, and increasing (Sengupta 1972; FAO 2008)

3.2.4.4 Inorganic Materials

There are several food-grade inorganic materials, which have been described as being useful for coatings or microencapsulation in food applications. They can be utilized alone or in combination with other materials. They include tripolyphosphate (CAS# 7758-29-4) (Desai and Park 2006), silicon oxides, or aluminum oxides (Amberg-Schwab et al. 2006).

3.3 Analytical and Characterization Methods

The suitability of a GRAS chemical substance for the encapsulation basically results from its molecular characteristics, i.e., the chemical composition, the molecular architecture, the molar mass, as well as the homogeneity/heterogeneity/

polydispersity of these characteristics. Exclusively, these molecular parameters govern all substance/material properties including solid material properties, behavior of melts and solutions, and molecular interactions. Therefore, despite the fact that industrial interest is primarily on material properties and their correlation with the properties of the final products, the knowledge of molecular characteristics and their correlation with material properties is a prerequisite for correct material selection and process optimization so as to obtain the desired texture and functionality in food products. Table 3.6 lists material properties, which are important for encapsulation materials, and molecular characteristics from which they result.

Carbohydrate polymers, proteins, and lipids are isolated and manufactured from natural resources. For the majority thereof, the chemical composition, structure, molecular dimensions, and homogeneity vary more or less, as discussed in Sect. 2 of this chapter. Such variation can complicate and render more difficult their application since sophisticated quality control procedures have to be performed continuously.

Due to the different chemical nature, molecular architecture, size, and physical properties of carbohydrates, proteins, and lipids, the three groups require rather different characterization methods and analysis techniques. Common to all is that separation and purification has to precede all analysis and characterization.

This section is not intended to provide comprehensive information about polysaccharide, protein, and lipid analysis and characterization. The reader is referred instead to appropriate specialist literature. Each of the materials discussed in Sect. 3.2 has its own peculiarities. Therefore, focus will be on practical aspects of methods and techniques and will be limited to polysaccharides, the dominating materials of this chapter.

The most frequent situation encountered is that the materials supplier provides more or less comprehensive basic information/specification about the particular substance that has been ordered. This information can be sufficient in many cases for established industrial applications though can be insufficient for research as well as product and technology development. The basic information is usually restricted to the chemical structure/composition, degree of purity, and the range of macromolecular characteristics.

Table 3.6 Substance and molecular characteristics of macromolecular encapsulation materials

Substance characteristics	Molecular characteristics
Solubility	Chemical composition
Rheology of melt and/or solution	– Sequence of monomer units
Transition temperatures (T_m, T_g)	– Homopolymer or heteropolymer
Stability (pH, T)	– Neutral or charged
Surface activity	Molecule architecture
Film forming ability	– Linear
Gelation ability	– Branched
Crystallinity	– Cross-linked
Density	– Linkage of monomer units
	Molar mass/molar mass distribution

Only for these basic characteristics, which are subject to variability and have practical relevance, will the appropriate analytical and characterization methods and procedures be considered here. Some characteristics, such as the type of monomer units and their linkage, do not change for a given polysaccharide even if the percentage or the molar mass varies. They can be taken as known without the need for repetitive examination.

3.3.1 Isolation and Purification

Polysaccharides suitable for encapsulation have to be isolated and purified prior to quantitative analysis and characterization. Impurities, which do not interfere with the practical application, can falsify analytical results. In addition, some of the materials presented here are mixtures of two or more components, which have to be analyzed separately. Also, the percentage of the components is of practical interest. Its variation may affect the rheological behavior, surface activity, or gelation behavior.

Purification methods are mainly based on physical characteristics of the macromolecules such as molecular size, charge, polarity, solubility, or specific interactions. Commonly used purification and separation techniques are: filtration, centrifugation, dialysis, preparative size exclusion chromatography, ion exchange chromatography, affinity chromatography, or electrophoresis.

3.3.2 Composition Analysis

The dramatic improvement of analytical methods during the last two decades, the increase of the sensitivity, precision, accuracy, and complexity, has contributed to a more comprehensive and better identification and quantitative determination of biopolymers. Nevertheless, the analysis of biopolymers still remains a challenge.

The composition analysis of polysaccharides (and also of proteins) requires chain degradation (chemical or enzymatic hydrolysis) as a first step, followed by separation of the monosaccharides released and their derivatives. Finally, the detection and quantification complete the analysis. Frequently, the separation, detection, and quantification are combined (Aspinall 1982), for example gas chromatography with mass spectrometry (GC-MS). Further applicable separation methods are: high-performance liquid chromatography (HPLC), capillary zone electrophoresis, and some methods already listed for purification above. Preferably, spectroscopic methods are used for the detection and quantification including UV-VIS, spectroscopy, infrared spectroscopy (IR, FTIR), and nuclear magnetic resonance (NMR) spectroscopic techniques. For specific composition analysis colorimetry, circular dichroism (CD), and polarimetry can be used. NMR has become the most powerful and non-invasive physicochemical technique for determining polysaccharide structure (Brummer and Cui 2006).

Electrochemical methods such as the acid-base titration, potentiometry, complex titration, and conductometry (Wandrey and Hunkeler 2002) are useful in both

identifying and quantifying charges in polysaccharides. These methods do not require degradation of the macromolecules.

Overall, the type of the biopolymer under investigation governs the selection of separation, detection, and quantification methods. Figure 3.21 illustrates the principal procedure of composition analysis.

3.3.3 Macromolecular Characterization

Macromolecular characterization methods serve to primarily determine the molar mass (MM) and/or the molar mass distribution (MMD). Commonly used absolute and relative methods are listed in Table 3.7, together with the parameters, which they deliver. Absolute methods, such as osmometry, analytical ultracentrifugation, light scattering techniques, or mass spectrometry directly yield the MM and/or the MMD. Relative methods, such as dilution viscometry, gel permeation chromatography/size exclusion chromatography (GPC/SEC), or field-flow fractionation (FFF) require previous calibration in order to obtain the MM or MMD. However, frequently the molecular separation techniques GPC/SEC and FFF are combined with detectors which yield directly information about the MM and MMD. Such coupled, hyphenated, and multidimensional procedures have become the state-of-the-art for the separation and analysis of macromolecules. In addition to information about the molecular dimensions, hydrodynamic, thermodynamic, and conformational information also become available. Analytical ultracentrifugation (AUC) is particularly suitable for the macromolecular characterization of polysaccharides (see e.g., Harding 2005).

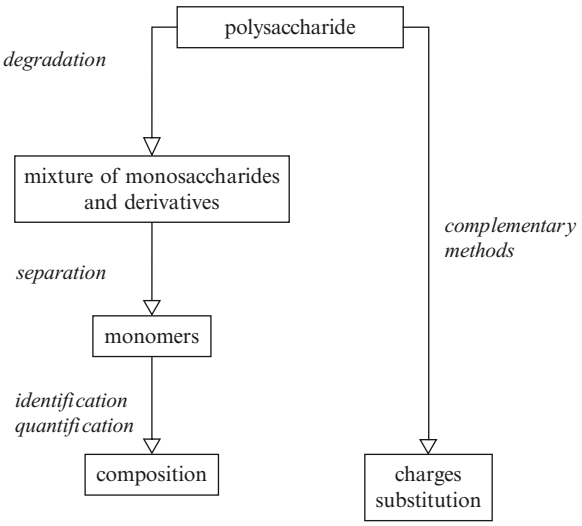

Fig. 3.21 Scheme for polysaccharide composition analysis

Table 3.7 Macromolecular characterization methods

Method	Direct	With calibration/fitting
Absolute methods		
Membrane osmometry	M_n	
Vapor pressure osmometry	M_n	
Analytical ultracentrifugation		
Sedimentation velocity	s, r_h	M_n, M_w, M_z, MMD
Sedimentation equilibrium	M_n, M_w	
Static (classic) light scattering	M_w, $<s^2>_z^{1/2}$	
Dynamic light scattering	D, r_h	M_d, MMD
Mass spectrometry	M_n, M_w, M_z, MMD	
Relative methods		
Dilution viscometry	$[\eta]$	M_v
GPC/SEC	V_e	r_h, MMD
Super critical fluid chromatography	V_e	MMD
Field-flow fractionation	V_e	r_h, MMD

GPC/SEC Gel permeation chromatography/size exclusion chromatography
M_n Number average molar mass
M_w Weight average molar mass
M_z z-average molar mass
MMD Molar mass distribution
s Sedimentation coefficient
r_h Hydrodynamic radius
D Diffusion coefficient
$<s^2>_z^{1/2}$ z-average root mean square radius
$[\eta]$ Intrinsic viscosity
V_e Elution volume

The macromolecular characterization of neutral polysaccharides can be performed, in general, in a two-component mixture, containing only the macromolecules and solvent. By contrast, the characterization of charged polysaccharides (polyelectrolytes) and proteins requires more efforts. Low molar mass salt/buffer has to be added to the aqueous solution for sufficient electrostatic screening, allowing the application of the usual characterization methods as for neutral macromolecules. Nevertheless, such multi-component mixtures remain more complicated. The electrostatic interactions, which interfere with the characterization, are suppressed but not removed.

3.3.4 Rheological Characterization

Since the rheological behavior of polysaccharides, proteins and lipids is of particular importance for encapsulation processes, some consideration of this is included in this chapter. Very often material suppliers specify macromolecular characteristics

in terms of the dynamic viscosity of a solution of defined concentration. This is critical since a solution containing a mixture of two narrowly distributed fractions, differing in the average molar mass, can have the same dynamic viscosity as a solution containing only one broadly distributed fraction. However, the rheological behavior will differ considerably.

Rheological measurements can also be very useful for facilitating the acquisition of knowledge about the molecular size, shape, solvent and macromolecular interactions, and intermolecular network formation. Certain polysaccharides even exhibit a very characteristic rheological behavior due to their particular molecular structure and composition. Nevertheless, there are also certain generalities of the rheological behavior.

The rheological behavior of polymer solutions or melts depends on both the molecular characteristics and the concentration. There is a strong interrelation. Of course, the medium conditions (temperature, pH, ionic strength, type of salt ions present) have an impact too, however, they can be manipulated for comparison. Different concentration ranges have to be distinguished: first, concentrated solutions where polymer molecules are entangled, not separated, and form a network; secondly, dilute solutions where polymer molecules are separated from each other and molecular dimensions depend on the chemical structure, the molar mass, the temperature, and the quality of the solvent. The transition occurs at the so-called critical polymer concentration or overlap concentration c*. Below c*, neutral polymers in very good solvents can still slightly expand, however, retaining their coil conformation. In the case of polyelectrolytes, such as charged polysaccharides the coil expansion is much pronounced and also the electrostatic atmosphere around polyelectrolyte molecules becomes more extended. Under certain conditions, the molecules approach a rod-like conformation. Overall, and under otherwise comparable conditions, the higher the molar mass, the stiffer the molecules, and the higher the charge density of the polymer, the lower is c*. Polysaccharide solutions normally exhibit Newtonian behavior at concentrations below c*, whereas above c* non-Newtonian behavior is usually observed.

To study the rheological behavior, dilution viscometry yielding the intrinsic viscosity and different techniques of rheometry are employed. The intrinsic viscosity, $[\eta]$, can be correlated with the molar mass in a Mark–Houwink relationship $[\eta] = KM^a$. The exponent a of such a correlation provides additional information about the macromolecular conformation.

Many polysaccharide solutions exhibit similar flow behavior at higher concentration. Frequently, Newtonian properties with a constant zero-shear viscosity over a limited shear range are observed at low shear rates. With increasing shear rate shear thinning occurs (pseudoplastic behavior), i.e., the solution viscosity decreases non-linearly. There are several rheological models to describe the flow behavior (Rao 1999).

Overall, to understand the correlation between chemical composition and molar mass on the one hand and the rheological behavior on the other hand, well purified and fractionated polysaccharide samples of low polydispersity have to be the subject of correlation studies. Even if such samples will never be used practically,

their study is necessary for identifying reliable basic correlations, which then will contribute to the product development and process optimization.

3.4 Regulatory Aspects

3.4.1 Safety Evaluation of Existing and Potential Encapsulation Materials as Food Additives

All food additives including microcapsules must have demonstrated useful purpose and undergo a rigorous scientific safety evaluation before they can be approved for use (Saltmarsh 2000). At an international level there is a Joint Expert Committee, from the Food and Agriculture Organization (FAO) and the World Health Organization (WHO), on Food Additives (JECFA). The JECFA has been in existence since 1955 and serves as a scientific advisory committee to FAO, WHO, Member Governments and the Codex Alimentarius Commission. Its principal role is to assess the human health risks associated with the consumption of additives to food and to recommend Acceptable Daily Intake (ADI) levels. The acceptable daily intake (ADI) approach to toxicological evaluation was initiated by the Joint FAO/WHO Expert Committee on Food Additives in 1961. The procedure involves collecting all relevant data, ascertaining the completeness of the available data, determining the no-effect level using the most sensitive indicator of the toxicity, the so-called "no-observed-adverse-effect level" (NOAEL), and applying an appropriate safety factor to arrive at the ADI for man. The ADI provides a large safety margin and is the amount of a food additive that can be consumed daily over a lifetime without any adverse effect on health.

The Codex Alimentarius Commission, a joint FAO/WHO activity which develops guidelines for food safety globally, is also drawing up new "General Standards for Food Additives" (GSFA), with the aim of establishing a harmonized, workable, and indisputable international standard for world trade. Only those additives that have been evaluated by the JECFA can be applied as food additives. Thanks to such strict regulation and thorough testing, food additives can be considered safe components in human diet that are contributing to the rapid evolution of the food supply throughout the world.

Each listed and accepted food additive specified by JECFA has its own specification card in the Compendium of Food Additive and Flavoring Agents Specifications (JEFCA 2008a), where all information and definitions related to the chemical composition, structure and properties are listed. Moreover, each card describes in detail common standardized identification methods and, more importantly, identifies purity requirements on an acceptable level of dry content, other chemicals including heavy metals, and specific microbiological criteria. Furthermore, from the 61st JECFA meeting even more specific information including the chemical and technological aspects of new or existing food additives are available to the public as Chemical and

Technical Assessment (CTA). The CTA reflects and emphasizes the role that the chemical characterization plays in the risk assessment of food additives. These documents provide basic information related to identity, purity, and use of the food additive, as related to its risk assessment. The CTAs are available at the FAO JECFA website (JEFCA 2008b) although there is no intention at present to publish in print. Furthermore, useful information on characterization methods and techniques provide the Combined Compendium of Food Additive Specifications "Analytical Methods, Test Procedures and Laboratory Solutions, which is referenced in the JECFA specifications" (JEFCA 2006).

In the EU, up until the creation of the European Food Safety Authority (EFSA), the safety evaluation of additives in Europe had been done by the Scientific Committee on Food (SCF). At present, it is the EFSA Panel on Food Additives, Flavorings, Processing Aids and Materials in Contact with Food (AFC Panel), who is in charge of this task. EU legislation requires studies investigating the range of intakes across a population and to address any changes in consumption patterns. Occasional intakes over the ADI are unlikely to cause any harm because of the 100-fold safety margin. In Europe, the market for food products is harmonized by several rules for authorization and conditions for the use of additives. In 1989, the European Community adopted a Framework Directive (89/107/EEC) (European Parliament and Council Directive 87/107/EEC 1988), which set out the criteria by which additives would be assessed and provided for the adoption of three specific technical directives: Directive 94/35/EC on sweeteners; Directive 94/36/EC on colors, and Directive 95/2/EC on additives other than sweeteners and colors (European Parliament and Council Directive 95/2/EC 1995). These three directives establish the list of additives, which can be used (to the exclusion of others), the foods in which they can be used and any maximum levels that are appropriate. The purity required for these additives is laid down in directives defining specific purity criteria.

Regulatory information associated with already established or potential materials, which can be used for encapsulation in the food sector (Table 3.8), is continuously updated on the web and provided in standard bibliographies (e.g., General Standard for Food Additives 1995; Codex Alimentarius 2008).

3.5 Strategies for the Selection of Materials

Besides energy and water supply, food is, and will remain, one of the three major fundamental topics for the continuation of mankind. However, the problems of fast-multiplying populations in developing countries causing lack of resources on the one hand and serious health problems in industrially developed countries due to wrong nutrition on the other, require innovative solutions. Moreover, increasing consumer health concerns associated with growing demand for healthier food is stimulating innovative and new product development in the food industry internationally. This development is an important factor for the expanding worldwide

Table 3.8 List of food additives with INS Numbers and ADIs already applied or with potential in encapsulation technologies (JECFA-Reviewed Food Additives) (General Standard for Food Additives 1995)

Name	INS/E[a] number	ADI[b]
Alginic acid	400	NS
Sodium alginate	401	NS
Potassium alginate	402	NS
Ammonium alginate	403	NS
Calcium alginate	404	NS
Propylene glycol alginate	405	70 mg/kg
Agar	406	NL
Carrageenan	407	NS
Locust/carob bean gum (LBG)	410	NS
Guar gum	412	NS
Gum tragacanth	413	NS
Gum arabic	414	NS
Xanthan gum	415	NS
Karaya gum	416	NS
Tara gum	417	NS
Gellan gum	418	NS
Curdlan	424	NS
Konjac flour glucomannan	425	NS
Pectins (amidated and nonamidated)	440	NS
Cyclodextrin, alpha	457	NS
Cyclodextrin, gamma	458	NS
Cyclodextrin, beta	459	5 mg/kg
Powdered cellulose	460ii	NS
Methyl cellulose	461	NS
Ethyl cellulose	462	NS
Hydroxypropyl cellulose	463	NS
Hydroxypropyl methyl cellulose	464	NS
Methyl ethyl cellulose	465	NS
Sodium carboxymethyl cellulose	466	NS
Ethyl hydroxyethyl cellulose	467	NS
Cross-linked sodium carboxymethyl cellulose	468	NS
Sodium carboxymethyl cellulose, enzymatically hydrolyzed	469	NS
Beeswax, white and yellow	901	A
Candelilla wax	902	A
Carnauba wax	903	7 mg/kg
Shellac	904	A
Microcrystalline wax	905ci	20 mg/kg
Gum benzoic	906	ND
Polydextrose A and N	1,200	NS
Insoluble polyvinylpyrrolidone	1,202	NS
Dextrins, white and yellow roasted starch	1,400	NS

(continued)

Table 3.8 (continued)

Name	INS/E[a] number	ADI[b]
Acid treated starch	1,401	NS
Alkaline treated starch	1,402	NS
Bleached starch	1,403	NS
Oxidized starch	1,404	NS
Enzyme treated starch	1,405	NS
Monostarch phosphate	1,410	NS
Distarch glycerol	1,411	ND
Distarch phosphate	1,412	NS
Phosphated distarch phosphate	1,413	NS
Acetylated distarch phosphate	1,414	NS
Starch acetate	1,420	NS
Starch acetate esterified with vinyl acetate	1,421	NS
Acetylated distarch adipate	1,422	NS
Hydroxypropyl starch	1,440	NS
Hydroxypropyl distarch phosphate	1,442	NS
Starch sodium octenyl succinate	1,450	NS
Acetylated oxidized starch	1,451	NS

[a]*INS/E* International Numbering and E-number systems for food additives. The INS was prepared by the Codex Committee on Food Additives and Contaminants for the purpose of providing an agreed international numerical system for identifying food additives in ingredient lists as an alternative to the declaration of the specific name. An E-number signifies approval of an additive by the EU. To obtain an E-number, the additive must have been fully evaluated for safety by the SCF or the European Food Safety Authority. E stands for edible

[b]*ADI* acceptable daily intake estimated by JECFA/OFAS based on animal toxicology or human studies; expressed as either a numerical value (mg/kg bw/day – body weight per day), or in general as *A* acceptable, *NL* not limited, *NS* not specified – very low toxicity, *ND* not determined

interest in the functional food (Lopez-Rubio et al. 2006). Therefore, the creation of novel functionalities of active ingredients in complex food matrices is of increasing importance for the food industry.

Traditional active ingredients are flavors, vitamins, and minerals. Relatively novel ones are probiotic microorganisms and various classes of bioactive compounds (Ubbink and Krüger 2006). Moreover, the food industry is aware of the potential of particle coating technology and has identified numerous potential applications for its use (Werner et al. 2007). Nevertheless, compared to the pharmaceutical industry and medical fields, the microencapsulation, coating and embedding of active ingredients is as yet much less used.

By analyzing the publications related to materials used for microencapsulation in the food industry, which are able to entrap/encapsulate ingredients in homogeneous matrices and/or capsules surrounded by protecting walls, one will realize that many, if not the majority, of these publications have been based on the

selection of materials on empirical grounds. Several materials and combinations are explored on a trial and error basis in order to identify the most suitable one. A strictly scientific selection starting with the analysis of the targeted application or product has rarely been reported. Nevertheless, principal strategies become obvious, namely selection of the material related to the technological requirement, selection considering the properties of the ingredient, or selection primarily oriented to the final product quality.

Of course, the application of microencapsulation in the food industry can have various goals such as the creation of a totally new product, improvement of an existing product, protection of a known ingredient, improvement of an existing process, replacement of an existing technology, along with others. All these aspects will also affect the strategies for the selection of a matrix/wall material. Nevertheless, the fundamental knowledge of the chemistry and physico-chemical properties of the materials will remain the prerequisite for successful product development. There is no substitute for the study and detailed analysis of the properties of potential matrix/wall material in order to conclude or predict its behavior under conditions present in food formulations. However, one has to be aware of the specific problems that may result from the use of natural materials, which can vary, within certain limits, from batch to batch. Serious restrictions may also result from economical aspects.

3.5.1 Use of Established Materials

A number of well-established industrial technologies for the microencapsulation of food ingredients including appropriate material description have been summarized and discussed in various review papers. A representative but not comprehensive list of such reviews is given here: Air-suspension particle coating in the food industry (Werner et al. 2007), Bioactive packaging: turning foods into healthier foods through biomaterials (Lopez-Rubio et al. 2006), Food protein-based materials as neutraceutical delivery systems (Chen et al. 2006), Physical approaches for the delivery of active ingredients in food (Ubbink and Krüger 2006), Flavor encapsulation and controlled release (Madene et al. 2006), Recent development in microencapsulation of food ingredients (Desai and Park 2005a), Liposomal nanocapsules in food science and agriculture (Taylor et al. 2005), Chances and limits of microencapsulation in modern food processing (Kruckeberg et al. 2003), Microencapsulation: industrial appraisal of existing technologies and trends (Gouin 2004), Cyclodextrins as food ingredients (Szente and Szejtli 2004), Technological challenges for future probiotic food (Mattila-Sandholm et al. 2002), Encapsulation in the food industry (Gibbs et al. 1999), Novel applications of liposomes (Lasic 1998), Fundamental aspects of controlled release in foods (Pothakamury and Barbosa-Cánovas 1995), Microencapsulation and the food industry (Jackson and Lee 1991).

Some of these papers include recommendations for the selection of materials. Tables 3.9 and 3.10 list recent microencapsulation studies with materials-oriented

Table 3.9 Examples of application of materials, which have been published recently

Active	Material for encapsulation	Technology	Comment	Reference
Vitamins				
Vitamin C, acerola, synthetic ascorbic acid	(a) Maltodextrin of DE20Mixture DE20/gum arabic (GA);		DE20/GA (3:1) most effective for vitamin C protection	(a) Righetto and Netto (2006)
	(b) Maltodextrin DE25, GA, or mix of both	(b) Spray-drying		(b) Righetto and Netto (2005)
Vitamin C	Tripolyphosphate/chitosan	Spray-drying	Process optimization	Desai and Park (2005b, 2006)
Vitamin E	Starch	High-pressure homogeniza-tion	Beverage fortification, nanoparticles	Chen and Wagner (2004)
Vitamin A acetate dissolved in coconut oil	hi-CAP 100 (starch octenylsuccinate, OSA-starch)	O/w emulsion, spray-drying	Effect of humidity	Xie et al. (2007)
Folic acid	Alginate-pectin	Coacervation	High efficiency: improved stability of folic acid during cheese ripening	Madziva et al. (2006)
Aroma/flavor				
European pear aroma	α-cyclodextrin (CD), GA, soybean soluble polysaccharide (SSPS), highly branched cyclic dextrin (HBCD)	Spray-drying, freeze-drying	Aroma content variation from 1.35 g/100 g with HBCD to 14.1 g/100 g with GA; MCs with α-CD and GA stable to 120°C	Tobitsuka et al. (2006)
	Cyclodextrins	Inclusion complexation	Fundamental data to obtain powdered pear flavor; best: α-CD	Tobitsuka et al. (2005)
Oregano, citronella, and marjoram flavors	Milk-protein based matrices: WPC, skimmed milk powder (SMP)	Spray-drying	Efficiency (% of flavoring entrapped in MC): 54.3% (marjoram in WPC) to 80.2% (oregano in SMP); particle size: 6–280 μm for SMP, 2–556 μm for WPC	Baranauskiene et al. (2006)

(continued)

Table 3.9 (continued)

Active	Material for encapsulation	Technology	Comment	Reference
Limonene	Gum arabic-sucrose-gelatin	Freeze-drying	1:1:1 most efficient	Kaushik and Roos (2007)
Cardamom oil	Mesquite gum	Spray-drying	High flavor retention of 83.6% for an oil: gum ratio of 1:4	Beristain et al. (2001)
Probiotics				
Bifidobacterium lactis	Hydrated gellan, xanthan gums	Extrusion	Suitable means for supplying viable probiotics to the food	McMaster et al. (2005)
Bifidobacterium PL1	Starch	Spray coating, spray-drying	Modified starch might not be suitable for use as an encapsulation material for probiotic strains	O'Riordan et al. (2001)
Lactobacillus acidophilusBifidobacterium. lactis	Alginate/Hi-Maize™ starch	Emulsion	Microencapsulation enhanced the survival of probiotic cultures compared to free cells in yogurts stored over 7 weeks, but negative influence on the textural properties	Kailasapathy (2006)
Lactobacillus. acidophilus 547B. bifidum ATCC 1994, Lactobacillus casei 01	Alginate/$CaCl_2$/chitosan		Survival of encapsulated bacteria was by about 1 log cycle higher	Krasaekoopt et al. (2006)
Bifidobacterium. breve R070Bifidobacterium. longum R023	Milk fat, denaturated whey proteins	Emulsion, spray-drying		Picot and Lacroix (2004)
Lactobacillus sp.	Gum arabic (GA), gellan gum (GG), mesquite gum (MG), and binary mixtures thereof	Interfacial polymerization	Highest viability in microcapsules of GA/MG mixtures	Yáñez-Fernández et al. (2008)
Lipids				
Conjugated linoleic acid (CLA)	Whey protein concentrate (WPC), gum arabic (GA), blend WPC/maltodextrin 10DE (1:1, w/w)	Spray-drying	WPC: best morphology and encapsulation efficiency, lowest CLA degradation	Jimenez et al. (2006)
Linoleic acid	Gum arabic	Spray-drying	Analysis of the oxidation process	Fang et al. (2005)

			best wall materials	(2006)
Lipids: oleic acid, linoleic acid, stearic acid	Potato starch, waxy maize starch, tapioca starch	Microwave heating	Facile process; formation of an amorphous matrix; no lipid interaction/reaction with starch matrix	Kapusniak and Tomasik (2006)
Oil				
Vegetable oil	Maltodextrin/GA, 3/2, w/w	Spray-drying + agglomeration in an air fluidized bed	Good oxidation protection; suitable floatability and wettability of the powders	Fuchs et al. (2006)
Fish oil	(a) Modified cellulose, skim milk powder, mixture of fish gelatin/corn starch	Spray-drying	(a) Changes in fish oil sensory quality; resulting powder was not stable; oxidized in the presence of air; stability may be improved when stored under vacuum	(a) Kolanowski et al. (2007)
	(b) Methylcellulose (MC), hydroxypropyl methylcellulose (HPMC), maltodextrin		(b) High oil retention; especially MC improved the stability and concentration in the powder	(b) Kolanowski et al. (2004)
	Modified starch	Spray-drying	Optimization of loading	Tan et al. (2005)
Tuna o/w emulsion	Lecithin-chitosan, corn syrup	Layer-by-layer deposition + spray-drying	Result: tuna oil droplets in a carbohydrate wall matrix; good physico-chemical properties	Klinkesorn et al. (2006)
Mixtures				
Ferrous sulfate + ascorbic acid	Liposomes	Pro-liposome and micro-fluidization	Size: about 5 μmSize: 150–200 nm Demonstration of the feasibility of microfluidization-based liposomal delivery systems for large scale food/nutraceutical applications	Kosaraju et al. (2006)
Iron (ferric pyrophosphate), iodine (potassium iodate), Vitamin A (retinyl palmitate)	Hydrogenated palm fat	Spray cooling	Microcapsules added to local salt in Morocco; highly stable microcapsules for salt fortification in Africa	Wegmuller et al. (2006)

(continued)

Table 3.9 (continued)

Active	Material for encapsulation	Technology	Comment	Reference
Others				
Chito-oligo saccharide	Polyglycerol monostearate (PGMS)		Application to commercial milk	Choi et al. (2006)
Anthocyanin pigments of black carrot	Maltodextrins: DE 10, DE 20-23, DE 28-31	Spray-drying	Best powder with DE 20–23	Ersus and Yurdagel (2007)
Isoflavone, β-galactosidase	Medium-chain triacylglycerol (MCT), polyglycerol monostearat (PGMS)		Both could be microencapsulated with fatty acid esters and released effectively in simulated intestinal condition	Kim et al. (2006)
allyl isothiocyanate – AIT (pathogens inhibitor)	Gum arabic		AIT microencapsulated in GA could be used in chopped refrigerated beef to reduce/eliminate *E. coli*	Chacon et al. (2006)
IgY	Whey protein concentrates (WPC-34, 50 and 80); whey protein isolate (WPI)	Emulsification, heat gelation	Effective for controlled IgY release to food systems	Lee et al. (2004)

Table 3.10 Examples of general applications of materials

Material	Application	Technology	Comment	Reference
Hybrid polymer coated with inorganic oxide layer (SiOx, AlOx)	Barrier against oxygen, water vapor, flavor permeation	Sol-gel	For food packaging	Amberg-Schwab et al. (2006)
Starch – linear amylose	Inclusion complexes with a wide variety of flavor compounds; controlled favor release	Complexation	Build-up and breakdown of starch flavor structures studied	Heinemann et al. (2005)
Whey protein concentrate 75	Soy oil	Spray-drying	Powders with oil content 20–75% (w/w)	Hogan et al. (2001a)
Sodium caseinate				Hogan et al. (2001b)
Beeswax, carnaubawax	Water-soluble compounds	Emulsion, solid or liquid preparation	Colorants	Mellema et al. (2006)

aspects. Table 3.11 reports about which materials can be used for which technology. This table may be regarded as an extension of Table 2.1 in Chap. 2. Often several materials are used in mixtures with other polymers. Therefore, some of the technologies listed in Table 3.11 may be applicable only if the appropriate material is mixed with others.

3.5.2 Identification and Definition of Criteria for Selection of a Material

The definition of the purpose of encapsulation is an important criterion for the selection of a material. The purpose could be, for example, the increase of shelf life, masking of taste, simplification of handling, guarantee of controlled and/or targeted release, or improvement of appearance. Answers to questions such as (Desai and Park 2005a):

- What functionality should the encapsulate provide to the final product?
- Are there restrictions for the coating material?
- Which concentration of the encapsulate has to be guaranteed?
- Which type of release is intended?
- What are the stability requirements?
- Are there cost constrains?

Table 3.11 Summary of the suitability of carbohydrate polymers, proteins, lipids, and a few other materials for principal technologies used for microencapsulation in the food industry

Material	Technologies
Starch and derivatives	Spray-drying, fluidized bed coating, extrusion, freeze-drying, microwave-assisted heating
– Maltodextrins	Spray-drying, fluidized bed coating, extrusion
– Syrups	Fluidized bed coating, extrusion, co-crystallization
– Cyclodextrin	Inclusion complexation (molecular inclusion)
Cellulose and derivatives (MC, HPMC, HPC, EMC, EC)	Spray-drying, fluidized bed coating, extrusion, emulsification/precipitation
– CMC	Coacervation, microwave-assisted encapsulation
Plant exudates (GA, GT, GK, MG)	Spray-drying, fluidized bed coating, extrusion, coacervation, freeze-drying
Plant extracts	
– Guar, LBG, tara	Extrusion, phase separation
– Pectins	Spray-drying, coacervation,
– SSPS	Spray-drying, freeze-drying
Marine extracts (carrageenans, alginate)	Spray-drying, extrusion, coacervation, emulsification
Microbial/animal extracts (xanthan, gellan, dextran, chitosan)	Spray-drying, coacervation, emulsification
Proteins	Fluidized bed coating
– Gluten	Spray-drying, coacervation, emulsification
– Caseins	Spray-drying, extrusion
– Whey proteins	Spray-drying, emulsification
– Gelatin	Spray-drying, extrusion, coacervation, freeze-drying
Lipids	
– Fatty acids and alcohols	Fluidized bed coating, spray chilling/cooling, extrusion, centrifugal suspension separation
– Glycerides	Spray chilling/cooling, extrusion, centrifugal suspension separation
– Waxes	Fluidized bed coating, extrusion, emulsification
– Liposomes	Liposomal entrapment
Others	
– PVP	Spray-drying
– Paraffin	Fluidized bed coating, spray chilling/cooling
– Shellac	Spray-drying
Inorganic	Sol-gel transition
– CO_2, N_2, water	Supercritical fluid technology

will further support the identification of a matrix or wall material.

Overall, materials for microencapsulation have to fulfill all or some of the following requirements (based on Desai and Park 2005a):

– Have good rheological properties at high concentration (if needed) and easy work ability during the encapsulation

- If applicable, disperse or emulsify the active material and stabilize the emulsion produced
- Do not react with the material to be encapsulated
- Seal and hold the active material within its structure during processing or storage
- If applicable, completely release solvent or other material used during encapsulation under drying or other desolvating conditions
- Provide maximal protection of the active against environmental conditions
- Are inexpensive
- Are food grade and legally allowed
- Are available at large quantities and constant quality

Depending on the ingredient, the process, and the application the requirements for the matrices may be different, requiring various shapes (films, spheres, irregular particles), or various structures such as compact or porous, amorphous or crystalline, rubbery or glassy. As an example, requirements for flavor encapsulation are: no reactivity with the core material, a form that is easy to handle (low viscosity at high concentration), complete elimination of solvent, maximum protection of the active ingredient, good emulsion stabilization properties, and effective redispersion behavior (Madene et al. 2006).

Ultimately, the approval of matrix/coating material by, for example, the FDA (US) or the European Food Safety Authority will govern the choice of material for microencapsulation in the food industry.

3.5.3 Strategies

After criticizing that the choice of technology and encapsulation material is often based on trial and error and not on a fundamental understanding of the physical and chemical phenomena determining the stability, release, perception, and digestion, Ubbink and Krüger (2006) proposed a strategy focusing on the desired functionality in the food product. The target application at the outset needs to be analyzed using scientific principles including materials science, physical chemistry, and biophysics. It is recommended to first precisely define the functionality and performance of the encapsulate in the final application, then to analyze the physical, chemical, and biological properties of the encapsulate and the conditions prevailing in the matrix/capsule. This includes identifying both the conditions required for maintenance of the performance of the ingredient and the limits to the conditions set by the properties of the matrix/capsule. It is emphasized that the functionality is defined solely based on the analysis of the interaction of the ingredient with the matrix/capsule and it does not relate at this stage to a specific technology. This concept/strategy of functionality postpones the selection of a technology to a later stage.

Werner et al. (2007) pointed out that the specific core and the ability of the coating material to impart the desirable characteristics to the product mainly

influence the choice of appropriate coating material. It is their opinion that, although the performance of the coating in the final application is crucial, the matching of the material to the process technology and process conditions is likely to be of equal importance, and yet is almost certainly overlooked in practice. Typically, a large number of coating materials must be tested in order to determine their suitability. There is a lack of knowledge about matching of encapsulate and matrix/capsule/coating properties. It was, therefore, concluded that in order to speed up the product development it is important to establish guidelines for polymer selection, and based not only on their performance in the final application, but also on their behavior in a coating process. There are attempts to predict coating properties based on physico-chemical properties of the coating materials, their hygroscopicity, viscosity, surface tension, and glass transition data. However, wet film properties rather than solution properties determine the coating quality. To understand the coating process, knowledge is required about the physico-chemical properties of both the coating solution and the films that form on these solutions as they dry (Dewettinck et al. 1998).

An example of a quantitative method for selecting the most suitable biopolymer has been given by Pérez-Alonso et al. proposing blends (Pérez-Alonso et al. 2003). The estimation of the activation energy of carbohydrate polymer blends provided a quantitative discrimination parameter for selecting the most suitable materials for protecting microencapsulated lipids against oxidative deterioration. However, no correlation with molecular parameters was considered.

Despite proposing various strategies/concepts for the appropriate selection of materials, which differ in some aspects, as demonstrated by the examples considered above, most of these strategies have in common the need for detailed analysis and correlation of the properties of ingredients or materials. There is no disagreement with this point. Interdisciplinary scientific developments at the interfaces between biomaterials science, physical chemistry, biophysics, and encapsulation technology will increasingly be incorporated (Ubbink and Krüger 2006) and will contribute to the progress of using microencapsulation in the food industry. In the biomedical field, the development of matrices for controlled release of bioactive substances (drugs) is already a fact and an active research area with constant improvement. This extensive knowledge gathered in the pharmaceutical and medical fields can be further exploited or rethought for the development of novel functional foods (Lopez-Rubio et al. 2006). Some limitations may, however, exist due to the use of not always food grade materials. But there is no doubt about the technological aspects.

3.6 Concluding Remarks

This chapter demonstrates that a variety of food-grade materials is in principle available for use for microencapsulation of food ingredients. The previous Chap. 2 reported a number of technologies that are useful and applicable for this purpose. The challenge consists in adopting the microcapsules containing the

active ingredients with a maximum of functionality to the whole food matrix. To achieve an optimum of the key functionality, which is usually determined by the barrier properties of the coating/film/matrix, a detailed knowledge of the chemical and physical properties of the food-grade encapsulation material is required. Due to the natural origin of the majority of these materials, a certain variability of the molecular characteristics and composition has to be taken into account. This requires defined specification controlled by sophisticated analysis and characterization. Further, the interaction between encapsulation material and ingredient deserves attention. Knowing the chemical nature of both may allow a priori conclusions. Nevertheless, for the final application, the properties of the coating/capsule/barrier formed by the carbohydrate polymers, proteins, lipids, their mixtures, or complexes are of particular importance. Because the microencapsulation technology and the final environment in the food may govern these properties, interdisciplinary collaboration is required for optimal solutions. Conclusions from studies, which establish basic correlations, will be favorable to support the development of food innovations. Apart from this, economical considerations will remain crucial for the selection of the most appropriate encapsulant materials.

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