Chapter 1
Introduction to Food Hydrocolloids

Wei Lu, Xiaobei Li, and Yapeng Fang

Abstract This introductory chapter provides an overview of the definition, classification, structure, market, regulation, and functional aspects of food hydrocolloids. The narrow and wide definition of hydrocolloids is compared. A detailed classification based on the source of hydrocolloids is summarized and the molecular structure of typical hydrocolloids, such as polysaccharides and proteins, is introduced. Food hydrocolloids show diverse potentials in the application of food, nutrition, and biomedicine industries. They can act as thickening agents, and form gels with controlled physical properties and functionalities. They can also be employed as stabilizers for various dispersions, and delivery carriers for bioactive ingredients. Besides, many hydrocolloids, e.g., whey proteins, or dietary fibers, possess potential health benefits and can provide basic and essential nutrients for maintaining human life activity. Furthermore, food hydrocolloids can be tailored into functional materials with advanced applications in food packaging, biomedical materials, bionanomaterials, polymer electrolytes, synthesis of inorganic nanoparticles, and removal of organic pollutants. The market and regulatory aspects of food hydrocolloids are also briefly reviewed.

Keywords Hydrocolloids · Definition · Classification · Structure · Functionality · Regulation · Safety

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1   History of the Term

The colloidal gels were first investigated by Thomas Graham (1861), who is widely regarded as the funder of colloid chemistry. He proposed a definition of substances based on their diffusive behaviors. According to his definition, colloids are slowly diffusing substances with very high molecular weight and specific structure. Between these colloidal substances, there exist "feeble forces" that holds them together in a solution. Graham also defined the colloidal state as a dynamical state of matter which may change into a crystalloidal status.

About half a century behind the foundation of colloid chemistry, Freundlich, Ostwald, and Weimarn proposed a new definition of colloids (Mokrushin 1962), which is different from that given by Graham. They defined colloids as any substances which are in the dispersed colloidal state. The molecular weight has no relation to the colloidal state by this definition. For example, the fine suspensions of gold, silver chloride, or sulfur can also be classified as colloidal solutions according to this definition. The cognition process on the rationality and limitation of these two definitions may be also considered as the development process of modern colloid chemistry.

It was reported that the term "hydrocolloid" derived from the Greek *hydro* "water" and *Kolla* "glue" (Wüstenberg 2015). First known use of *hydrocolloid* can be dated back to 1916, which was used to describe a substance that yields a gel with water. Hydrocolloids are now defined as various long-chain polymers which can form viscous dispersions and/or gels when dispersed in water. These polymers can be found in extracts from seaweeds, exudates from trees, flours from grains, products from fermentations, and many other natural products. They contain many hydroxyl groups, which significantly increase their hydrophilicity making them hydrophilic compounds. Furthermore, they can create a dispersion, which is between a true solution and a suspension and show colloidal properties. In consideration of these two properties, they are termed as "hydrophilic colloids" or "hydrocolloids."

2   Definition

A narrow definition of hydrocolloids refers to a series of polysaccharides and proteins that are widely used in different industrial sectors to perform various functions including thickening and gelling agents, stabilizers of food dispersions (e.g., foams or emulsions), encapsulation and delivery carriers of functional ingredients and their controlled release (Phillips and Williams 2009). Besides, all soluble starches, which chemically belong to the polysaccharide family, can also be considered as a class of hydrocolloids with many potential applications in the food sector.

Hydrocolloids can also be broadly defined as a variety of biopolymers, biopolymer-stabilized dispersions, and biopolymer-based gels and particles, such as polysaccharides, proteins, lipids, protein/polysaccharide aqueous dispersions,

emulsions (including Pickering emulsions), foams, bubbles, protein/polysaccharide-based hydrogels and micro/nanoparticles, solid lipid nanoparticles, liposome, and oleogels.

3 Classification

Hydrocolloids are widely used in a variety of industries to perform different functions as described above (Williams and Phillips 2009; Lin et al. 2012). The frequently used hydrocolloids and their origins are given in Table 1.1.

Some of the plant hydrocolloids come from trees and tree gum exudates (e.g., cellulose, gum Arabic, gum karaya, gum ghatti, gum tragacanth) while some of them come from plant (cellulose pectin, and starch), seeds (locust bean gum, guar gum, tara gum, tamarind gum, soybean proteins, zein, rice protein, and gluten), and tubers (konjac glucomannan). Algal hydrocolloids are mainly derived from red seaweeds (agar, carrageenan, and furcelleran) and brown seaweeds (alginate).

Microbial hydrocolloids can be produced from simple sugars (glucose or sucrose) or starch using a microbial fermentation process. Species of bacteria and fungus that have been used to produce these hydrocolloids by fermentation include *Xanthomonas campestris* (xanthan gum), *Leuconostoc mesenteroides* and *Streptococcus mutans* (dextran), *Agrobacterium* (curdlan), *Athelia rolfsii* (scleroglucan), *Sphingomonas elodea* (gellan), and *Aureobasidium pullulans* (pullulan).

Animal-sourced hydrocolloids mainly are proteins coming from collagen taken from bones, skin, and tendons of animals, and skins of fish (gelatin), milk (caseinate and whey proteins), eggs (egg white proteins), and chitin shells of shrimps and other Crustaceans (chitosan).

Table 1.1 Source of frequently used hydrocolloids

Source	Hydrocolloids
Plant	*Polysaccharides* Starches, pectins, cellulose, larch gum, guar gum, locust bean gum, tara gum, tamarind seed gum, acacia gum/gum, Arabic gum, tragacanth, karaya gum, ghatti gum, inulin, and konjac glucomannan *Proteins* Soy proteins, zein, rice proteins, and gluten (wheat protein)
Algal	Alginate, carrageenan, agar, and furcelleran
Animal	Gelatin, caseinate, whey proteins, egg white proteins, glycogen, and chitosan
Microbial	Dextran, xanthan, scleroglucan, curdlan, pullulan, and gellan
Modified	Modified starches, propylene glycol alginate, microcrystalline cellulose (MCC), amidated pectin, methylcellulose (MC), ethylcellulose (EC), hydroxypropylmethylcellulose (HPMC), hydroxypropyl cellulose (HPC), and carboxymethylcellulose (CMC)

4 Structures

4.1 *Polysaccharides*

The primary molecular chain structure of polysaccharides is monosaccharide units (Table 1.2) bound together by glycosidic bond, which is formed between the hemiacetal or hemiketal group of a monosaccharide and the hydroxyl group of neighboring monosaccharide, known as O-glycosidic bonds. Besides, S-, N-, or C-glycosidic bonds also exist, where the oxygen of the glycosidic bond is replaced with sulfur, nitrogen, or carbon, respectively. In addition, α- or β-glycosidic bonds can be distinguished by the relative stereochemistry (R or S) of the groups of C5 and C1 in the pyranose ring. If groups connected to these two carbons have the same stereochemistry, the glycosidic bond is defined as α type, whereas a β-glycosidic bond is formed when the groups show different stereochemistry.
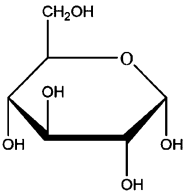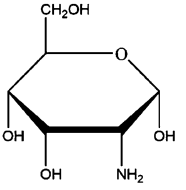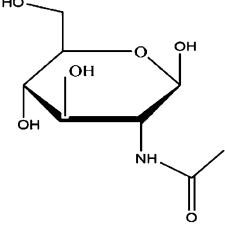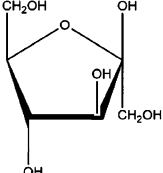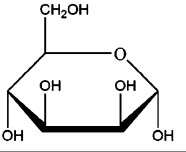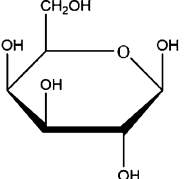
Therefore, glycosidic bonds in the backbone of polysaccharides mainly include α-1,4 (e.g., amylose, glycogen, amylopectin), β-1,4 (e.g., pectin, alginate, cellulose, guar gum, xanthan, konjac glucomannan, xylan), α-1,6 (e.g., dextran), β-1,3 (e.g., Arabic gum, laminarin), and β-1,2 (e.g., inulin) glycosidic bonds (Fig. 1.1). The backbone of some polysaccharides also shows a mixture of the different glycosidic bonds. For example, carrageenan is composed of repeating sulfated and/or non-sulfated galactose and 3,6-anhydrogalactose units. The units are linked by alternating α-1,3 and β-1,4 glycosidic bonds. A similar chain structure can be observed for gellan gum, which is made up of repeating tetra-saccharides consisting of two glucose and one of each residue of rhamnose and glucuronic acid.

Polysaccharides composed of the same monosaccharide are called homo-polysaccharides such as starches and glucan while those composed of more than one type of monosaccharides are called heteropolysaccharides. Some polysaccharides show a segmented chain structure. Alginic acid (Fig. 1.2), for example, is a linear biopolymer composed of β-1,4 linked D-mannuronate (M) and L-guluronate (G) residues. G and M resides are covalently linked together in different sequences or blocks. They can appear in consecutive M-residues (M-blocks), consecutive G-residues (G-blocks), or alternating M and G-residues (MG-blocks).

Besides, several polysaccharides show a crystalline zone in their chain structure, e.g., cellulose, or starch. The crystalline fractions of these polysaccharides with different structures and properties can be collected by physical or chemical processing such as microcrystalline cellulose (MCC), microfibrillated cellulose (MFC), and nanocrystalline cellulose (NCC). Furthermore, the chemical structure of natural polysaccharide is modified to improve its water solubility or functionalities. Examples include modified starch, propylene glycol alginate, amidated pectin, methylcellulose, ethylcellulose, or carboxymethylcellulose.
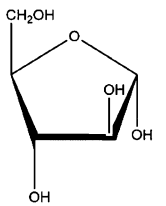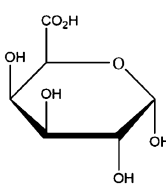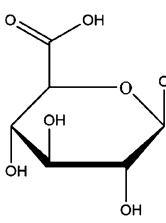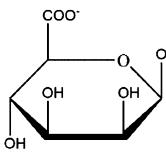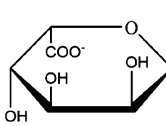
In direct analogy with proteins, polysaccharides can also have several levels of structures. The primary structure of a polysaccharide is defined as the sequence of monosaccharides. The intramolecular single helices with different persistence lengths are considered as secondary structures of a polysaccharide while tertiary

Table 1.2 Examples of common monosaccharides and corresponding polysaccharides

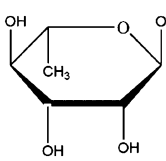| Monosaccharide	Molecular structure	Representative polysaccharides
Glucose		Starch, cellulose, β-glucan, konjac glucomannan, gellan, dextran, pullulan, xanthan, xyloglucan
Glucosamine		Chitosan
Acetyl-glucose		Chitosan Poly-N-acetyl-β-D-glucosamine
Fructose		Inulin
Mannose		Konjac glucomannan, guar gum, tara gum, fenugreek gum, locust bean gum, xanthan
Galactose		Arabic gum, guar gum, carrageenan, agar, tara gum, fenugreek gum, acacia gum, karaya gum, xyloglucan, locust bean gum

Table 1.2 (continued)

Monosaccharide	Molecular structure	Representative polysaccharides
Arabinose		Arabic gum
Galacturonic acid		Pectin
Rhamnose		Gellan
Glucuronic acid		Gellan, xanthan
Mannuronate		Alginate
Guluronate		Alginate

structures always exhibit as tight or loosely supercoiled helices. Tightly or loosely intertwined chains with tertiary structures form the intermolecular quaternary structures of polysaccharides (Fig. 1.3).

Diener et al (2019) demonstrated several structural levels using carrageenan as model polysaccharides. In the presence of potassium, a disorder to order the transition from random coil to single helix (secondary structure) was first observed,

	Cellulose	Starch		Glycogen
		Amylose	Amylopectin	
Source	Plant	Plant	Plant	Animal
Monose	β-glucose	α-glucose	α-glucose	α-glucose
Glycosidic bonds	1-4	1-4	1-4 and 1-6	1-4 and 1-6
Diagram				
Shape				

Fig. 1.1 Examples of molecular chain structure of polysaccharides
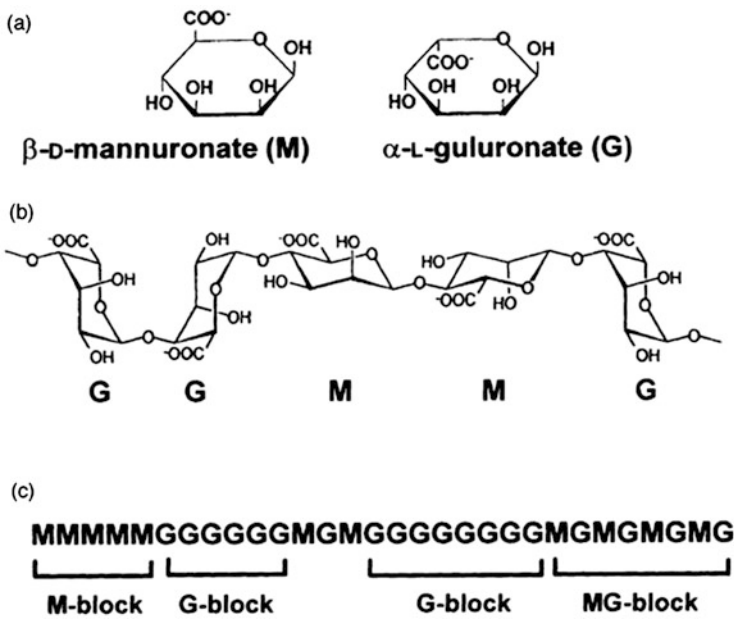
Fig. 1.2 Structural characteristics of alginates: (**a**) monosaccharide composition (**b**) chain conformation, (**c**) block distribution (Draget and Taylor 2011). The permission for reproduction of the figure was obtained from Elsevier
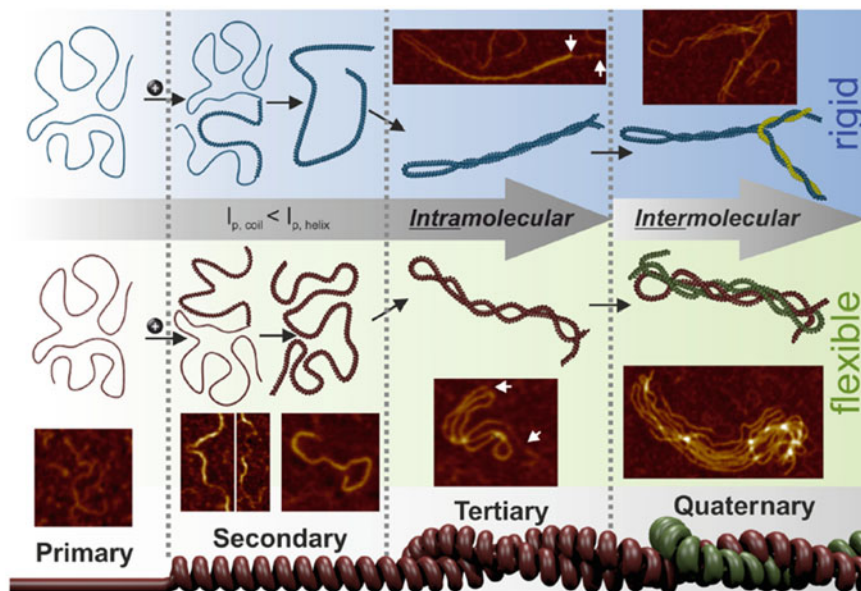
Fig. 1.3 Schematic elucidation of the multilevel structure of polysaccharide chains: An example from carrageenan (Diener et al. 2019). The permission for reproduction of the figure was obtained from ACS Publications

followed by intrachain supercoiling events (tertiary structure) and macroscopic anisotropic domains, which are part of a network (quaternary structure) with tunable elasticity up to ~10^3 Pa. Loosely intertwined helices were also observed as tertiary structure.

4.2   Proteins

Proteins are biopolymers comprised of one or more chains of amino acid residues. The amino acid residues in protein chains are linked together by peptide bonds, which is an amide-type of the covalent chemical bond linking C1 of one α-amino acid and N2 of another adjacent amino acid (Fig. 1.4).

Protein structure mainly refers to four distinct aspects (Finkelstein and Ptitsyn 2016): (1) primary structure, the amino acid sequence; (2) secondary structure, repeating structures formed by hydrogen bonds, mainly including α-helix, β-sheet, and β-turns; (3) tertiary structure, the spatial shape of a polypeptide chain or the spatial arrangement of the secondary structures. Tertiary structure is mainly stabilized by hydrophobic interactions, but also involving disulfide bonds, hydrogen bonds, salt bridges, or post-translational modifications; and (4) quaternary structures,
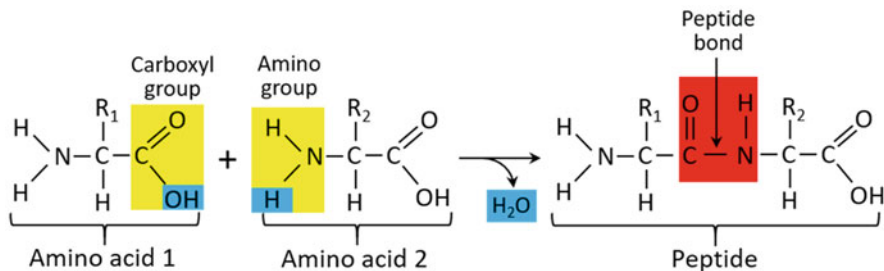
Fig. 1.4 Diagram of the formation and structure of peptide bond

the structure formed by several polypeptide chains (technically termed as protein subunits) (Robert et al. 2009).

Proteins are not completely rigid molecules. Proteins may transform between the above-mentioned structures while they perform their functions. Generally, the tertiary or quaternary structure of proteins is regarded as their conformation, which is defined as the spatial arrangements of atoms. The conversion between different conformations generally does not refer to the breakage or formation of covalent bonds. For example, the structure of protein molecules can be altered by thermal vibration (thermal denaturation) or the collision with other molecules (Christopher et al. 2013). Thermal denaturation is also one of the mechanisms that induce the gelling of protein molecules in solutions. Conformation is different from another relevant term named configuration, which mainly refers to the fixed three-dimensional relationship of the atoms in a molecule, defined by the bonds between them. The change of configuration of proteins may involve the break or formation of covalent bonds, e.g., the change of primary and/or secondary structure of proteins (Finkelstein and Ptitsyn 2016).

5 Marketing

The lifestyle changes, the increasing awareness of the association between diet and health, and emerging new processing technologies contribute to a rapid increase in the consumption of food hydrocolloids-based ready-made, functional, and healthy food products, which consequently leads to an increase in the market demand of hydrocolloids. The market demand for hydrocolloids is estimated at $ 8.8 billion in 2018 and is predicted to grow at a compound annual growth rate (CAGR) of 5.3% from 2018 to 2023, to reach $ 11.4 billion by 2023 (Singh 2019). North American is predicted to be the fastest-growing market in these 5 years (Fig. 1.5).

The rising demands for convenient food products in the countries of the Asia Pacific, South America, and the Middle East & African regions promote the development of the processed food industry worldwide, which accordingly leads to a growth in the hydrocolloids market. In addition, manufacturers always focus on the
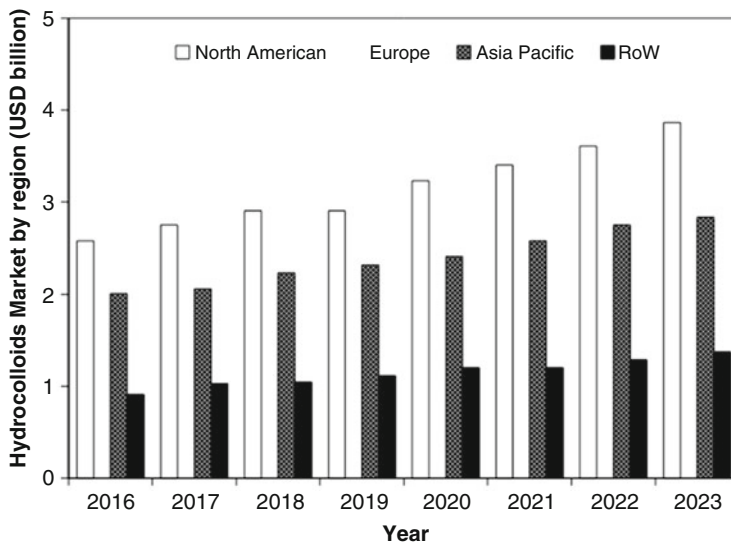
Fig. 1.5 Hydrocolloids market by region. RoW indicates the rest of the world (Singh 2019). The data from 2019 to 2023 is predicted based on the estimated growth rate

product innovation and multifunctionality of hydrocolloids with the objective of offering high-quality hydrocolloids for the end-users. Thus, manufactures perform various research and development (R&D) activities and these activities accordingly contribute to the rapid growth of the hydrocolloids market. One of the major factors that restrict the development of the hydrocolloids market is the international regulations and quality standards of food additives (e.g., stabilizers). The fluctuations in the price of raw materials for producing hydrocolloids can also affect the market.

In 2018, the thickeners sector, animal sector, food & beverage and gelatin sector are estimated to account for the largest share based on functions, sources, applications, and types of hydrocolloids, respectively. Take gelatin as an example, gelatin has wide applications in food products such as desserts, candies, ice creams, and marshmallows. In Europe, gelatin is classified as food and is not subjected to food additive legislation, which creates a lucrative opportunity for manufacturers in the next few years.

6 Legislation and Safety

6.1 Background

Food hydrocolloids, such as pectin, agar, starch, and gelatin, have been used for centuries, and consumers are quite familiar with these hydrocolloids. Many hydrocolloids in use today were developed long before regulatory approvals, and their use

level and use in specific applications were restricted. For instance, carrageenan, agar, or alginate extracted from seaweeds are eaten as basic foods. These edible polymers from seaweeds are thus considered safe for use in food products. This principle of "generally recognized as safe" (GRAS) is still in use today but under a more rigorous review. For example, carrageenan can be classified into λ-, κ, and ι-, carrageenan. Some of the modified carrageenan, e.g., semi-refined version, found its way of being used as food texturizing agent only since the 1980s and 1990s while refined carrageenan has been used for more than 60 years (Imeson 2010). However, intentional acid-hydrolyzed carrageenan, like poligeenan, cannot form gels and even have been proved to cause in vivo gastrointestinal ulceration and tumors via food, water, or oral route. Poligeenan has been also reported to show immune system toxicity and potentially suppress the immune response (McKim et al. 2018). These results suggested that degraded fractions of nature hydrocolloids which can be safely used as food additives need strict safety evaluation before being used in the food industry.

6.2 Legislation

Regulatory approval of a food ingredient is necessary because the additives would have no function or market without approval by the governments. Food hydrocolloids are generally regulated either as a food additive or as a food ingredient. Except for gelatin, most of the food hydrocolloids are currently regulated as food additives.

Regulatory authorities strictly control the approval of food additives (Imeson 2010). Chemical modifications are generally not allowed except for cellulose derivatives, starches, and propylene glycol alginate. Physical and enzymatic modifications are allowed, e.g., physically modified pectin (Slendid™, CP Kelco Division of JM Huber). Some new hydrocolloids are brought to the market under the "generally recognized as safe" principle, such as konjac, tara gum, and pullulan. Gellan gum is the last hydrocolloid that completely goes through a food additive petition in the global market. It took many years and cost tens of millions of dollars to get the approval of gellan gum. The total profit earned by gellan gum over the next 20 years after its approval is still lower than the cost for its approval. These probably suggest that it is almost impossible for a new hydrocolloid to accomplish a full approval process in the global market in the foreseeable future. Cassia gum has recently been approved in France (August 2008) and it is expected to be approved in the EU market soon.

6.2.1 International System

The Food and Agriculture Organization (FAO) and the World Health Organization (WHO) established the Codex Alimentarius Commission (CAC) in 1962. CAC is an intergovernmental organization consisting of delegations from FAO and WHO

member countries that take part in developing the food standards. Another organization, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) was established before the CAC in 1956 (Magnuson et al. 2013), which is considered as the oldest and most active body in doing a similar job.

The main task of CAC is to address the safety and nutritional quality of food products and to develop international standards for promoting trade of foods, such as setting standards for approved food additives, determining its limits of addition and safety indexes (e.g., limits for contaminants and toxins, and residue limits for pesticides), and establishing hygiene and technological function practice codes. These standards, guidelines, practice codes, and recommendations constitute the Codex Alimentarius.

6.2.2 European System

European Commission first cleared food hydrocolloids in 1995 based on the Directive 95/2/EU for Food Additives, which is known as the Miscellaneous Additives Directive (MAD). MAD authorized a large number of food hydrocolloids (including alginates, starches, celluloses, and most gums) for their utilization in food products at suitable levels (Phillips and Williams 2009). Since the adoption of the Directive, the Commission proposed several modifications by considering the development of the market. A second modification was made in 1998 and the Member States of the EU were required to put into effect this updated version in 2000. The new regulation in this Directive (98/72/EC) came into force in all EU Member States and it affected many hydrocolloids, mainly including potassium alginate, sodium alginate, konjac, carrageenan, guar, and pectin.

6.2.3 US and Japan Systems

Since the CAC is the final regulation and can provide for worldwide approvals, countries (outside the EU) are free to adopt their standards. In United States (USA), the Food and Nutrition Board of the Institute of Medicine (funded by the United States Food and Drug Administration, FDA) published the Food Chemicals Codex (FCC), and the regulation about hydrocolloids can be found in the Fourth Edition pressed in 1996. Japan also has its own regulation system, including many food additives specific to Japan (Dai and Chau 2017).

6.2.4 China Systems

In China, except for starch, the usage of hydrocolloids in foods is regulated by "National standards for food safety: standards for the use of food additives (GB2760)," which was first established in 2011 (GB2760-2011), and then modified in 2014 (GB2760-2014). It stipulates the type of hydrocolloids that can be used in

China and their levels in the products. Based on GB2760-2014, around 40 hydrocolloids are allowed to be used in the China market. For example, the most widely used hydrocolloids in meat and fish products include carrageenan, xanthan gum, guar gum, agar, gelatin, alginate, locust bean gum, curdlan, and konjac glucomannan. These frequently used hydrocolloids are all naturally derived.

Generally, these edible hydrocolloids are used at a low level, mainly functioning as thickening agents, stabilizers, and gelling agents. Many hydrocolloids can also be considered as dietary fibers, which have many potential health benefits. Thus, a low level of using edible hydrocolloids in food products is always safe or even good for health. However, some manufacturers use a high level of hydrocolloids for specific purposes (cost, stability, etc.), leading to a potential safety issue of the products. In addition, many hydrocolloids can also be used in industrial products, and industrial-grade hydrocolloids are much cheaper than food grade, but potentially contain various harmful ingredients, which can threaten human health. Therefore, it is illegal to use industrial-grade hydrocolloids in food products but it still can happen that some producers illegally add them into foods due to their low cost.

6.3 Consumer Concerns

No matter what the scientific facts are, it is the consumers' approval that decides the market future of a food ingredient, and hydrocolloids are no exception. In terms of perception, a label is very important. A friendly label always can reduce people's perception of too much chemical connotation, and thus feel they are safe. For example, label-friendly carbohydrate gum and vegetable gum are used to describe methylcellulose and hydroxypropylmethylcellulose in the USA, respectively. Another example, carboxymethyl cellulose (CMC) is a very chemical name, whereas cellulose gum, a synonym of CMC, sounds much more acceptable. Therefore, EU authorities allow the use of cellulose gum on the label.

Another main concern is genetic engineering and relevant genetically derived hydrocolloids. For example, seeds, seaweed, or other plants could be genetically modified to yield a higher production of relevant hydrocolloids; kelp could be edited to produce more alginates; the mature time of a carob tree that can produce a commercial scale of bean gum could be significantly shortened as compared with the normal 12–15 years. However, the safety of these genetically derived hydrocolloids is not conclusive, and their application is still constrained by consumer concerns (Imeson 2010).

Table 1.3 Hydrocolloids commonly used in food applications

Applications		Hydrocolloids
Structuring agents	Thickening agents	Xanthan, methyl cellulose (MC), carboxymethyl cellulose (CMC), guar gum, hydroxypropylmethyl cellulose (HPMC), locust bean gum, konjac glucomannan, tara gum, and xyloglucan
	Gelling agents	Amylose, agar, carrageenan, gellan gum, pectin, alginate, casein, soybean proteins, gelatin, xanthan, MC, HPMC, locust bean gum, konjac glucomannan, xyloglucan, and curdlan
Stabilizers	Emulsifiers	Gum Arabic, modified starch, modified cellulose, crystalline cellulose, pectins, galactomannans, casein/caseinate, whey proteins, and soy proteins
	Foaming agents	Casein, whey proteins, zein, gelatin, pectins, modified cellulose, chitin, and chitosan
Delivery carriers	Nanoparticles, films, fibrils, microcapsules, hydrogels particles	Whey proteins, casein, gelatin, zein/gliadin, agar, carrageenan, alginate, chitosan, guar gum, cellulose, pectin, xanthan gum, and starch
Bioactive ingredients	Dietary fibers, antimicrobial, anti-virus, anti-coagulant, antioxidant, anti-cancer, reducing blood lipids, enhancing the immune system and bone health, anti-cardiovascular disease, lowering blood pressure, losing weight, satiating effect	Resistant starch, cellulose, hemicellulose, guar gum, pectins, β-glucans, psyllium; sulfated polysaccharides from marine algae (e.g., sulfated fucoidan, carrageenan, galactans, fucoidan, sulfated rhamnogalactans, laminaran, and alginic acid), and whey proteins
Advanced materials	Food packaging, biomedical materials, scaffolds, biomimetic materials, nanostructured membranes, electrolytes, decontamination materials	Starch, modified cellulose, chitin/chitosan, pectin, gluten, soy proteins, gelatin, zein, crystalline cellulose, and crystalline starch

7 Functionality and Application

Hydrocolloids can be functionally used as the thickening and gelling agents, stabilizers for emulsions and foams, and delivery carriers for bioactive components. They can be also tailored into advanced nanomaterials with various specific applications in both food and biomedical industries. Besides, hydrocolloids and their derivate show diverse health benefits and are considered as a class of bioactive ingredients. In this section, these main functionalities of hydrocolloids are summarized (Table 1.3).

7.1 Structuring Agents

Hydrocolloids have been used in a variety of food formulas to improve their quality and shelf-life. The two major applications of hydrocolloids are thickening and gelling agents. Regarding the thickening, they have been used in many food systems, such as gravies, soups, sauces, salad dressings, and toppings. In terms of gelling, hydrocolloids can be used in products like jelly, jam, marmalade, low-calorie gels, or restructured foods.

7.1.1 Thickening Agents

The process of thickening refers to the entanglement of polymer chains, leading to a significant increase in the viscosity of the system. Thickening occurs above a critical polymer concentration (overlap concentration, C^*), which refers to the transition from the "dilute region," where the polymers can move freely without entanglement in solution, to the "semi-dilute region," where molecules crowding promotes the overlap of polymer coils and thus leads to the entanglement. Below C^*, the polymer dispersions exhibit Newtonian behavior whereas shows a non-Newtonian behavior above this concentration (Phillips and Williams 2009).

The viscosity of the polymer solution is significantly affected by the molecular mass of the polymer. The dependency of viscosity on the shear rate increases with the increasing molecular mass. When the molecular mass of the polymer increases, the shear thinning of the polymer dispersion occurs at a lower shear rate value. In addition, the hydrodynamic size of polymers can be obviously influenced by their molecular structures. Linear and stiff molecules always show a larger hydrodynamic size than that with a branched and flexible structure and thus yield a much higher viscosity (Phillips and Williams 2009).

Hydrocolloids that have been applied as thickening agents include starch, gum Arabic or acacia gum, modified starch, xanthan, gum tragacanth, galactomannans, gum karaya, and CMC (Saha and Bhattacharya 2010) (Table 1.4). The thickening effect of hydrocolloids can be influenced by many factors, including the type of hydrocolloids used, concentration, pH, temperature, or the food system in which they are used.

7.1.2 Gelling Agents

Gels are a form of matter intermediate between solid and liquid states, showing both elastic (mechanical rigidity) and flow (liquid) properties (Aguilera 1992). A sol (liquid) to gel (solid) transition occurs when gels are formed. Gelation is the process that the polymer chains crosslink to form a three-dimensional (3D) network that entraps water within it (Oakenfull and Glicksman 2009). Food hydrocolloids are widely employed as gelling agents to produce food gels with acceptable properties,

Table 1.4 Hydrocolloids used as thickeners in foods

Hydrocolloids	Properties	Applications
Xanthan	Highly shear thinning; keeps viscous at high temperature and wide pH ranges	Soups and gravies, ketchup, beverages, toppings, desserts, and fillings
CMC	High viscosity; decreased viscosity by adding electrolytes and at low pH	Gravies, salad dressings, ketchup, and fruit pie fillings
MC and HPMC	Viscosity increases with increasing temperature; viscosity is independent of pH and electrolytes	Cake batters, beverages, salad dressings, and whipped toppings
Gum Arabic	Low viscosity; shear thinning dispersion at low shear rates (<10/s); near Newtonian behavior above the shear rate of 100/s	Soft drinks and fruit juice based beverages
Galactomannans (guar gum, locust bean gum and tara gum)	High viscosity at low shear rate; highly shear thinning; the viscosity is independent of electrolytes; decreased viscosity at very high and very low pH, and high temperatures	Dairy products, i.e., ice cream, ketchup, fruit juices, pudding powder, and cake batter
Konjac glucomannan	Highly viscosity independent of salts; forms thermally irreversible gels in the presence of alkali	Noodles, jelly desserts, surimi, meat products
Xyloglucan	Heat, acid, salt resistant, short texture (non-thread forming)	Sauce for grilled eat, cutlet
Gum tragacanth	Rehydrates fast in cold or hot water to produce highly viscous dispersion, up to 4000 mPas at 1 w/w%	Salad dressing, bakery emulsion, fruit beverage, and sauce

especially the texture properties (Table 1.5). Food gels are 3D network structures of high moisture. Food gels can resist flow under pressure and retain their distinct shape. They are viscoelastic systems with a storage modulus (G') larger than the loss modulus (G'') (de-Vries 2004).

Many classifications can be done for gels (See Chap. 4). Gels formed by covalent bonds are called chemical gels, and those formed by secondary bonds such as hydrogen bonds, electrostatic and hydrophobic interactions, and/or van der Waals forces are called physical gels (Djabourov et al. 2013). Gels can be formed by physical (e.g., heat or pressure), chemical (e.g., pH), or biological treatments (e.g., enzymes). For example, milk gels can be formed by acid or by rennet, while KGM gelation is induced by alkali. However, some physically induced gels, for example by heating, can make covalent bonds and thus lead to the formation of chemical gels. The gel formation always depends on several physicochemical factors, including temperature, pressure, ionic strength, pH, presence of enzyme, solvent quality, the concentration of gelling agents, selection of different biopolymers and their molecular weight (Banerjee and Bhattacharya 2012). Selection and control of these factors result in the formation of different kinds of gels, such as hydrogels, organogels, xerogels, aerogels, emulsion gels, oleo gels, weak gels, fluid gels, or temperature-sensitive gels (thermoreversible or thermo-irreversible) (Graham et al. 2019). Gels

Table 1.5 Hydrocolloids used as gelling agents

Hydrocolloids as a gelling agent	Properties	Applications
Modified starch	Cold-set gel; thermal irreversible and opaque	Dairy desserts
Agar	Cold-set gels; thermoreversible	Bakery products, jellies
κ-, and ί-Carrageenan	Cold-set gels; thermoreversible	Puddings, milk shakes, tofu
Low methoxy pectin	Cold-set gels at low pH; thermoreversible	Jams, glazes, jellies, milk-based desserts
High methoxy pectin	Cold-set gels at low pH; thermal irreversible	Jams, jellies
Gellan gum	Cold-set gels; thermoreversible; highly transparent	Jellies with different flavors
Alginate	Thermal irreversible gels; stable when being heated	Restructured foods, bakery creams
Methyl and hydroxypropylmethyl cellulose	Thermoreversible gels; instable when being chilled	Cake batters, beverages, whipped toppings, salad dressings
Curdlan	Thermoreversible and thermal irreversible gels	Surimi, sausage

with a wide range of properties can be obtained depending on the conditions that are employed for gel formation. Some gels are brittle, i.e., fractures at a small deformation, while the others are deformable and would not break even at very large deformation. They can be transparent or also be opaque.

7.2 Stabilizers

Hydrocolloids are widely used as stabilizers of food dispersions such as emulsions and foams, which can be used to design a variety of functional food structures with desired properties in texture, stability, flavor release, or nutrition.

7.2.1 Emulsifier

Hydrocolloids-based emulsifiers can be seen in many food products include carbonated ice cream, soft drinks, and sauces. Many hydrocolloids are able to act as stabilizers (stabilizing agents) of oil-in-water (O/W) emulsions, whereas only a few of them can act as emulsifiers (emulsifying agents). Emulsifying agents are required to have surface activity at the oil–water interface, and thus the ability to adsorb to the surface of newly formed oil droplets during homogenization, leading to

the formation of stable O/W emulsions (Dickinson 2009). Emulsifying activity and emulsion stability should be briefly described here as is done for foaming ability later.

The commonly used polysaccharide-based emulsifiers are Arabic gum, sugar beet pectin, modified starches, galactomannans, and modified celluloses. The emulsifying ability of these polymers has their chemical structure bases in either (1) the non-polar chemical groups attached to the molecular backbone (e.g., propylene glycol alginate, or hydrophobically modified starch/cellulose) or (2) the presence of a protein component covalently-, or physically linked to the polysaccharide (e.g., Arabic gum, sugar beet pectin, or guar gum).

Bovine milk and egg proteins are the most widely used protein-sourced emulsifiers such as casein and whey protein. Casein is a group of amphiphilic proteins which can be classified into α_{s1}-, α_{s2}-, β-, and κ-casein dependent on their sensibility to free calcium ion. Whey protein contains a family of globular proteins with rigid structures, mainly including α-lactalbumin, β-lactoglobulin, bovine serum albumin (BSA), and immunoglobulins. Animal-sourced gelatins (bovine, pig, or fish) also have amphiphilic characters, and show surface activity, but they typically exhibit a poor stabilization effect towards emulsions. Recently, the development of plant-sourced protein-based emulsifiers is receiving more and more attention, which is mainly driven by the vegetarian's will of replacing animal proteins to reduce the consumption of animal proteins, as well as to promote food sustainability and security. Some plant proteins are promising emulsifiers, including lupin proteins, pea proteins, corn germ proteins, and soy proteins (Ozturk and McClements 2016).

7.2.2 Foaming Agent

Foam is a dispersion where a high-volume of gas is dispersed in a liquid. The stabilization of foams requires an interfacial barrier to prevent coalescence of neighboring gas bubbles, e.g., the protein layer at the air–water interface. Food particles at the air–water interface can also stabilize or destabilize foams, depending on their properties (e.g., wettability or spreading). Foaming properties generally refer to the foaming capacity and foam stability. Foaming capacity (or foamability) is the capacity for the continuous phase to embed gas while the foam stability is defined as the ability to maintain the gas for a certain time. Many food-derived hydrocolloids have been widely used as stabilizers of foams, including casein, whey proteins, zein, gelatin, pectin, cellulose, chitin, and chitosan (Dickinson 2017). The foaming properties of hydrocolloids, e.g., proteins, depend on the intrinsic factors (e.g., chemical structure, size, hydrophobicity, or surface chemistry) and external factors (e.g., concentration, pH, temperature, and the presence of other components).
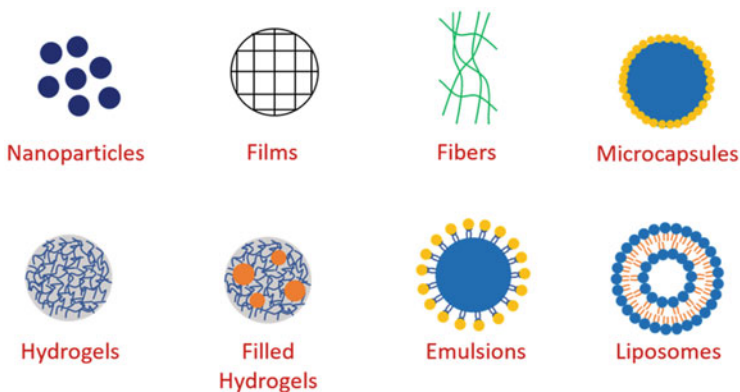
Fig. 1.6 Summarized functional delivery systems based on hydrocolloids

7.3   *Delivery Carriers*

Proteins and polysaccharides are two important kinds of biopolymers employed to fabricate food-grade delivery systems. They are biocompatible, biodegradable, and non-toxic polymers, which makes them attractive building units for delivery systems in food, biology, and medicine applications. In addition, the diversity of molecular structures exhibited by proteins or polysaccharides (e.g., molecular weight, branched or linear structure, charges, polarities, amphiphilicity, dimensions, or reactivities) offers researchers the opportunity to build delivery carriers with desired specifications (McClements 2016). These protein- or polysaccharide-based delivery carriers can be prepared by bottom-up methods that involve self-assembly of individual molecules into large particles, or top-down methods that involve breaking-down of large biopolymers into small fragments. Multiple intermolecular forces usually take part in the formation and stabilization of these carriers for bioactive components including electrostatic interaction, hydrophobic effect, hydrogen bond, steric repulsion, and/or van der Waals attractive force.

Proteins and polysaccharides commonly used to fabricate delivery carriers can be classified into water-soluble and water-insoluble ones. Water-soluble proteins and polysaccharides include casein, whey protein, agar, gelatin, carrageenan, alginate, pectin, guar gum, and xanthan gum while water-insoluble ones have zein, chitosan, gliadin, starch, or cellulose. Functional delivery carriers developed based on these biopolymers exhibited different structures, e.g., nanoparticles, films, fibers, hollow microcapsules, emulsions, or hydrogel particles (Fig. 1.6), through which a variety of nutraceuticals were delivered, such as polyphenols, vitamins, carotenoids, unsaturated fatty acids, fish oils, or essential oils (Abd El-Salam and El-Shibiny 2012; Ezhilarasi et al. 2012; Fathi et al. 2014).

7.4 Bioactive Ingredients

Except for the above-mentioned functionalities, many food hydrocolloids also show potential health benefits. For example, whey proteins and their derivate show a variety of health benefits, including antimicrobial and antiviral properties, and enhance immune defense and bone health, and protect against cancer and cardio-vascular disease, and reduce oxidative stress and increase levels of glutathione, and lower blood pressure, and potentially decrease the low-density lipoprotein (LDL) and blood cholesterol level, moderate blood sugar and increase both the level of insulin and the sensitivity of its effects, reduce inflammation, have beneficial effects on inflammatory bowel disease, and induce satiety and reduce hunger, and potentially help to lose weight (Birsen Bulut and Nihat 2012). Many of these health benefits can be attributed to bioactive peptides released by intestinal hydrolysis of whey proteins, e.g., antimicrobial peptides, angiotensin-converting enzyme (ACE) inhibition peptides, antioxidant peptides, or blood-sugar-control peptides.

Polysaccharides have been also reported to possess a variety of health benefits. One of their major health benefits is being considered as dietary fibers, which can positively generate a series of biological activity (Fig. 1.7), including but not limited to eliminating constipation or stimulating colonic muscular activity, encouraging stool expulsion, promoting the level of short-chain fatty acids (SCFAs), gastrointestinal peristalsis, inhibiting the population of pathogenic bacteria (*Clostridia*), acting as prebiotics (diet fibers) and antimicrobial agents, and reducing the lipid absorption (Mudgil and Barak 2013; Makki et al. 2018). Dietary fibers are a family of polysaccharides, and can be further divided into insoluble and soluble forms (Deehan et al. 2017). The definition of "soluble" and "insoluble" is different in the nutritionist community and physicochemical community. This is a serious problem. KGM is usually classified as a soluble dietary fiber by nutritionists, but physicochemists struggle to dissolve KGM. It depends on the acetyl content. If the acetyl group is introduced artificially, the solubility is improved. But some natural KGM is not so soluble. Water-insoluble dietary fibers such as cellulose and hemicellulose have a fecal bulking effect and are hard to be digested by the gut bacteria. However, water-soluble fibers can be fermented by the gut bacteria and release health-beneficial metabolites such as SCFAs. Furthermore, many soluble non-starch polysaccharides such as guar gum, pectin, β-glucans, and psyllium, can form a gel structure in the intestinal tract which can delay the absorption of glucose and lipids (Deehan et al. 2017).

In addition to dietary fibers, polysaccharides also show a variety of potential health benefits. Sulfated polysaccharides derived from marine algae, for example, are reported to possess many biological activities, including anti-coagulant, anti-virus, antioxidant, immunomodulation, inducing osteoblastic cell differentiation, protecting gastric mucosa against acid and pepsin, inhibiting UV-B induced matrix metalloproteinase-1 activity in human skin, and reducing cholesterol and triglycerides (TG) levels (Wijesekara et al. 2011). These health benefits of sulfated
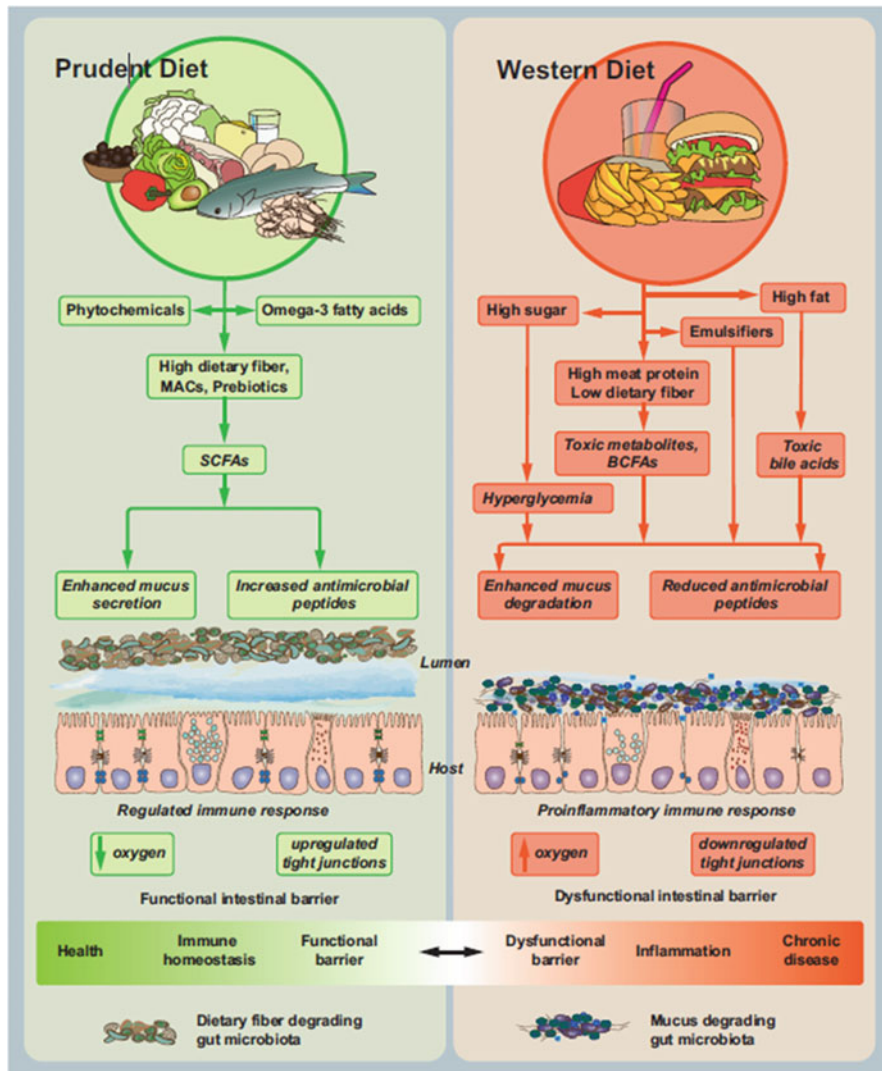
Fig. 1.7 Influence of low- and high-fiber diet on the composition, diversity, and function of gut microbiota (Makki et al. 2018). The permission for reproduction of the figure was obtained from Cell Press

polysaccharides are always correlated to their molecular structure, such as molecular weight.

Another attractive health benefit of polysaccharides is their great potential in reducing the risk of cancer. Many studies, mainly observational, have investigated the correlation between fiber intake and the risk of colon or rectum cancers. Intervention studies have confirmed the impact of dietary fiber on the recurrence

of adenoma, which are often considered an early marker of colorectal cancer. Nevertheless, there is no hard evidence that can prove the reducing-effect of fiber intake on the risk of colorectal cancer. Thus, the guideline on dietary fiber intake aiming to reduce the colorectal cancer risk seems to be lacking enough evidence but individuals with a low level of fiber intakes potentially have an increased cancer risk (Mudgil and Barak 2013).

7.5 Functional Materials

In addition to the above-mentioned functionalities, many food hydrocolloids can also be tailored into a variety of functional materials, such as food-packaging film, artificial joint prosthesis, bone tissue engineering materials, and cartilage tissue engineering (Kapoor and Kundu 2016).

7.5.1 Food-Packaging Materials

Foods are generally packaged to extend their shelf-life and to illustrate the composition and nutrition information to the consumers. With the increasing concern on the environmental and food safety requirements, the development of renewable biodegradable food-packaging materials raises more and more attention over the last few years, and a class of natural biopolymer-based materials has been developed as promising food-packaging materials. The food-derived biopolymers that were used to develop food-packaging materials can be classified into two major groups, polysaccharides and proteins. Polysaccharide-based packaging materials include starch, cellulose, chitin/chitosan, konjac glucomannan, and pectin while protein-based materials mainly have soy protein, wheat gluten, corn zein, gelatin, whey proteins, and casein (Tang et al. 2012).

Polysaccharide-based food-packaging films have different characteristics depending on the materials (Cazón et al. 2017): (1) Starch-based food-packaging materials always have moderate oxygen barrier properties but poor moisture barrier and mechanical properties; (2) Chemically modified cellulose derived packaging materials always show good moisture barrier properties, and are suitable for baked goods, fresh products (e.g., meat, fish, vegetables, fruits), processed meats, cheese, and candy. Esterified cellulose-based materials are excellent for high moisture foods as it allows respiration and reduces fogging; (3) Chitin/chitosan-based materials have clear, tough, flexible, and good oxygen barriers properties but poor long-term stability and low water vapor barrier properties; (4) Pectin based packaging material possesses high water vapor permeability, which limits its use in food packaging.

Different protein-based packaging materials also have their specific properties: (1) Gluten-based materials show good oxygen barrier properties but poor carbon dioxide (CO_2) barrier properties, which makes them possible to act as packaging materials for specific applications, e.g., mushrooms; (2) Soy protein-based materials

are always brittle and show poor water resistance; (3) Films formed by gelatin do not have good mechanical properties, even reinforced by several techniques, which thus limits their application as a packaging material; (4) Zein films always showed similar tensile strength but higher oxygen permeability as compared with gluten films. This is attributed to an easier diffusion of oxygen across the helical structure of zein as compared with the highly cross-linked structure of wheat gluten (Cazón et al. 2017).

Furthermore, nanocomposites based on the above-mentioned polysaccharides and proteins have also been developed as food-packaging materials, including starch-kaolin, starch-clay, cellulose acetate-clay, pectin-montmorillonite (MMT), gluten-MTT, gelatin-MMT, and SPI-MMT. These nanocomposites based packaging materials show improved tensile strength, thermal stability, and water/oxygen barrier capacity as compared with those produced by sole polysaccharides or proteins (Tang et al. 2012).

7.5.2 Biomedical Materials

Inorganic particle based biomedical nanomaterials can cause cytotoxicity owing to their accumulation, aggregation, decomposition, and/or generating reactive oxygen
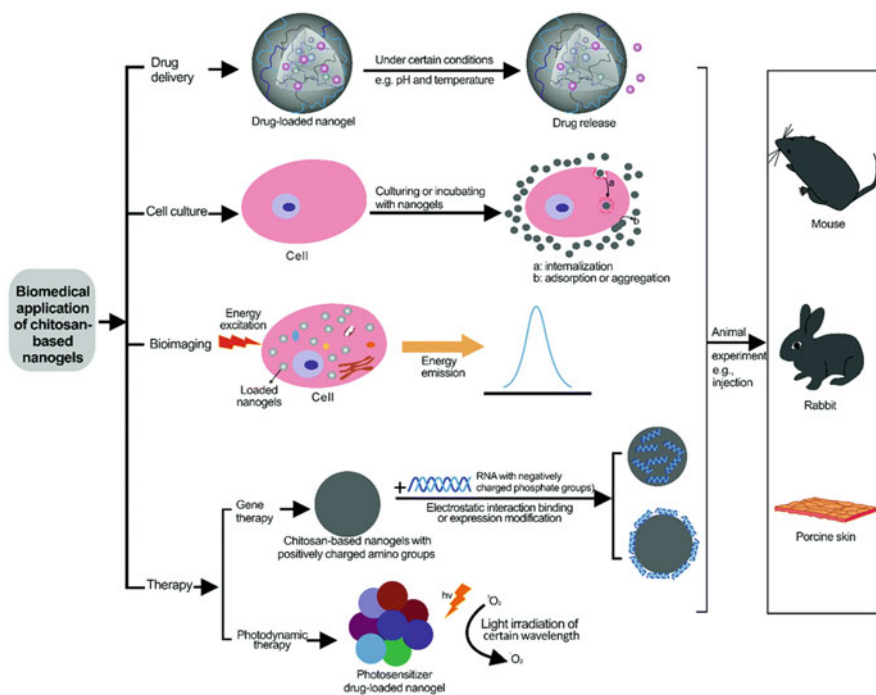

Fig. 1.8 Biomedical applications of chitosan-based nanogels (Wang et al. 2017). The permission for reproduction of the figure was obtained from Royal Society of Chemistry

species inside the cell. However, natural biopolymers, such as food polysaccharides and proteins, always have good biocompatibility and biodegradability, and they can be developed as functional and eco-friendly advanced materials. Food-derived biopolymers can be developed into diverse kinds of biomedical materials (Fig. 1.8). The biopolymers that have been employed to produce these advanced biomedical materials include chitin/chitosan, cellulose/nanocrystals, hyaluronan, gelatin, silk proteins, and whey proteins.

For example, polysaccharides nanocrystal can be developed into a variety of biomedical materials, such as electrolytes, nanoscaffolds, nanosponges, various biomimetic materials, cellular bioimaging materials, permselective membranes, and templates for the synthesis of inorganic nanoparticles (Lin et al. 2012). Natural polysaccharide nanocrystals potentially have prolonged retention in the circulation
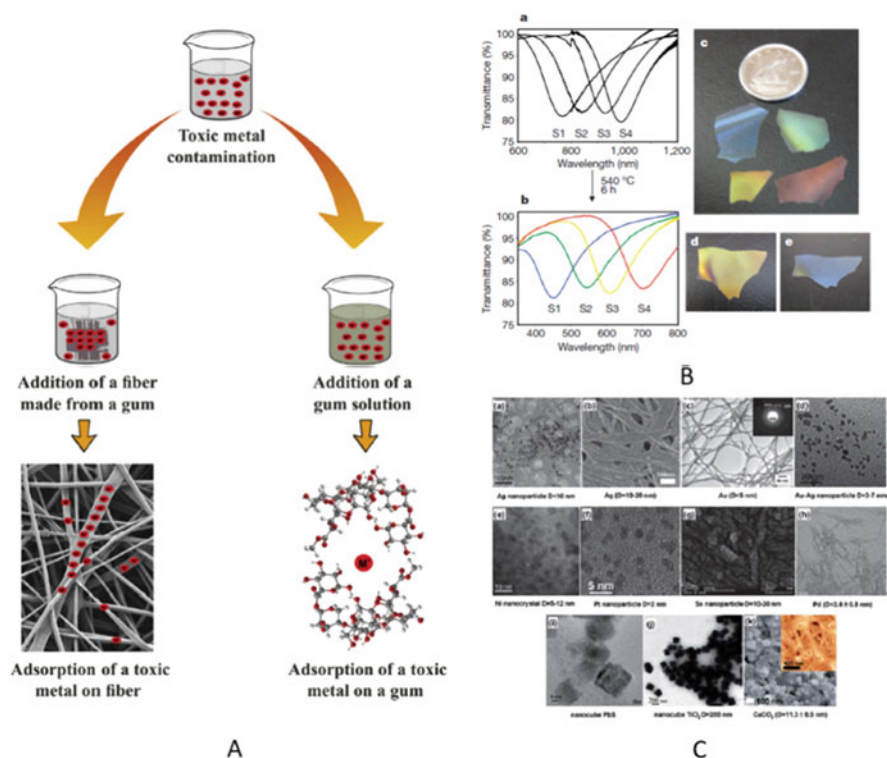

Fig. 1.9 Several hydrocolloids-based advanced materials (**a**) adsorption of toxic metal on gum fibers (right) and gum (left) (Padil et al. 2018). The permission for reproduction of the figure was obtained from Elsevier. (**b**) nanocrystalline cellulose-based biomimetic optical nanomaterials with a peak reflected wavelength of covering the entire visible spectrum (Shopsowitz et al. 2010). The permission for reproduction of the figure was obtained from Springer Nature. (**c**) morphology observation of inorganic nanoparticles prepared using cellulose nanocrystal as the template (Lin et al. 2012). The permission for reproduction of the figure was obtained from Royal Society of Chemistry

system, rendering them a promising biomedical material that is biodegradable and safe for the environment and human health.

7.5.3 Template for Synthesizing Inorganic Nanoparticles

Many hydrocolloids, e.g., cellulose nanocrystal (Fig 1.9c), can act as a template or scaffold of synthesizing inorganic nanoparticles. For example, mesoporous silica nanoparticles can be successfully fabricated by using rod-like cellulose nanocrystal as the template (Dujardin et al. 2003; Gruber et al. 2011). The cellulose crystalline based materials have also been used as the template for producing gold (Au), silver (Ag), uranium (U), palladium (Pd), platinum (Pt), selenium (Se), Au-Ag, Ag-Pd, cadmium sulfide (CdS), zinc sulfide (ZnS), lead sulfide (PbS), and titania (TiO_2) nanoparticles. The reduction reaction between the template and metal ions is the main mechanism for producing these nanoparticles, and the utilization of cellulose nanocrystal as the template can produce stable and high-density particles with a controlled size distribution, and significantly improve their chemical properties.

7.5.4 Other Types of Functional Materials

Food hydrocolloids can also be developed into many other types of advanced materials, such as mesoporous biomimetic optical nanomaterials with a peak reflected wavelength of covering the whole visible spectrum or even into the near-infrared by simple modification (Shopsowitz et al. 2010) (Fig 1.9b), bio-inspired mechanically adaptive nanomaterials used as adaptive substrates of intracortical microelectrodes (Shanmuganathan et al. 2010), nanostructured membranes with potential permselective function to differently charged substances (Thielemans et al. 2009), reinforced polymer electrolytes with high ionic conductivity and good stability (My Ahmed Said Azizi Samir et al. 2004), and decontamination materials of removing organic pollutants (Namazi and Dadkhah 2010) or toxic metal (Padil et al. 2018) (Fig 1.9a).

8 The Future Trends

Over the last half a century, great progress in the science and technology of food hydrocolloids was gained along with the rapid development of the food industry. Food hydrocolloids carry the flavor, texture, processing, nutrition, and health characteristics of foods and thus play an essential role in the food industry. In view of an increasing concern of consumers in a healthy way of life, both scientists and consumers pay more and more attention to the functionality of food products. The health benefits of food hydrocolloids have been revealed one after another. Nevertheless, the physiological activities of many emerging natural polysaccharides or

proteins have not been clarified. Furthermore, food hydrocolloids can potentially contribute to the future food structure design due to their ability in acting as structuring agents, e.g., elderly food, special diet food for diabetics, and low-salt foods, controlled-textured-flavored-foods for dysphagia. Moreover, excellent plasticity and mechanical properties of food hydrocolloids-based advanced materials make them possible to have promising applications in food, chemical, and biomedical industries, such as controlled or target delivery carriers of bioactive nutrients and drugs, meat analogue, artificial muscles, artificial joints or cartilage, or electronic elements. All in all, the food hydrocolloids market continues to see robust growth and the prospect of the future is worth to be expected.

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