



Review

Approaches in biotechnological applications of natural polymers

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Abstract: Natural polymers, such as gums and mucilage, are biocompatible, cheap, easily available and non-toxic materials of native origin. These polymers are increasingly preferred over synthetic materials for industrial applications due to their intrinsic properties, as well as they are considered alternative sources of raw materials since they present characteristics of sustainability, biodegradability and biosafety. As definition, gums and mucilages are polysaccharides or complex carbohydrates consisting of one or more monosaccharides or their derivatives linked in bewildering variety of linkages and structures. Natural gums are considered polysaccharides naturally occurring in varieties of plant seeds and exudates, tree or shrub exudates, seaweed extracts, fungi, bacteria, and animal sources. Water-soluble gums, also known as hydrocolloids, are considered exudates and are pathological products; therefore, they do not form a part of cell wall. On the other hand, mucilages are part of cell and physiological products. It is important to highlight that gums represent the largest amounts of polymer materials derived from plants. Gums have enormously large and broad applications in both food and non-food industries, being commonly used as thickening, binding, emulsifying, suspending, stabilizing agents and matrices for drug release in pharmaceutical and cosmetic industries. In the food industry, their gelling properties and the ability to mold edible films and coatings are extensively studied. The use of gums depends on the intrinsic properties that they provide, often at costs below those of synthetic polymers. For upgrading the value of gums, they are being processed into various forms, including the most recent nanomaterials, for various biotechnological applications. Thus, the main natural polymers including galactomannans, cellulose,

chitin, agar, carrageenan, alginate, cashew gum, pectin and starch, in addition to the current researches about them are reviewed in this article.

Keywords: agarose; alginate; carrageenan; chitin; galactomannan; gum; hydrocolloids; mucilages; polysaccharides; starch

1. Introduction

Natural polymers are materials of natural origin with properties of biocompatibility, low cost, availability and lack of toxicity. These polymers, such as gums and mucilages, are increasingly preferred over synthetic materials due to their intrinsic properties; in addition to be considered alternative sources of raw materials for industrial applications.

As definition, gums are polysaccharides composed by multiple sugar units linked together to create large molecules with heterogeneous composition. Upon hydrolysis, they yield simple sugar units such as arabinose, galactose, glucose, mannose, xylose or uronic acids. The polysaccharide gums represent one of the most abundant industrial biomaterials and have been reported by several studies due to their sustainability, biodegradability and biosafety. Gums are abundant in nature and commonly found in many higher plants; in addition, they are frequently produced as a protection mechanism following plant injury [1].

Besides gums, the constituents of polysaccharides also include mucilages. Although their natural polymeric source, gums and mucilages have certain differences: gums readily dissolve in water, while mucilages form viscous masses; gums are considered pathological products, whereas mucilages are physiological products. In addition, their similarities are related to their broad range of physicochemical properties, which are widely used for applications including cosmetics, paper, pharmacy, textile, adhesive, inks, lithography, paint, explosive, and smoking products [2,3]. In order to avoid misinterpretations, it is important to distinguish the above-mentioned terms.

Mucilage is a polysaccharide mixture commonly found in various organs of many higher plant species. Due to its high variability in terms of chemical constituents, mucilage probably assumes a multitude of physiological functions in plants [4]. Mucilages found in rhizomes, roots and seed endosperms may act primarily as energy reserves [5], whereas foliar mucilages appear not to serve as storage carbohydrates. Generally, it has been assumed that foliar mucilages are merely secondary plant metabolites, but there was also reported that they may play a role in wound responses, frost tolerance, water transport, plant host-pathogen interactions, the ionic balance of plant cells, and as carbohydrate reserves. There is growing evidence that, due to the high concentration of hydroxyl groups in the polysaccharides, extracellular mucilages in particular have a high water-binding capacity and may play an important role in the drought resistance of certain plant species [2].

Natural gum is a term used to describe a group of naturally occurring polysaccharides. They have widespread industrial applications due to their ability either to form the gel, make the viscous solution or stabilize the emulsion systems [6]. Water-soluble gums are described as hydrocolloids; they are used for various applications, including dietary fibers [7], texture modifiers, stabilizers and/or emulsifiers [8,9], gelling agents [10], thickeners [11], coating agents [12,13] and packaging films [14]. Many natural gums form three dimensional interconnected molecular networks known as “gels”. The strength of the gel depends on its structure and concentration, as well as on factors such as temperature,

pH, and ionic strength. The linear polysaccharides occupy greater volume than branched polymers of comparable molecular weight. Thus, at the same concentration, comparable linear polysaccharides exhibit greater viscosity. Therefore, it is difficult for the heterogeneous gum molecules to move freely without becoming entangled with each other (and any other large molecules also present). In addition, natural gums are often recognized by their swelling properties, which occurs due to the entrapment of large amounts of water between their chains and branches [1].

Cellulose, chitin, agar and starch are the most common polysaccharides used in industry. Regarding their broad range of applications, the preference for use of natural polymers is presumed over comparable synthetic materials due to their non-toxicity, low cost and availability. For instance, most of the natural gums are safe enough for oral consumption in the form of food additives or drug carriers [1]. In addition, synthesizing natural polymers as nanomaterials enhances the industrial applicability due to its larger surface, besides the intrinsic properties above mentioned. The present work considers the most recent literature dealing with natural polymers, including natural gums and mucilages, and their potential biotechnological applications. Moreover, we summarized information about their chemical structure, physicochemical and functional properties.

2. Classification of natural polymers and their biotechnological applications

Gums and mucilages are sourced from the endosperm of plant seeds, plant exudates, tree or shrub exudates, seaweed extracts, fungi, bacteria, and animal sources, where they perform a number of structural and metabolic functions; it is important to highlight that plant sources provide the largest amounts of gums. Natural gums are categorized based on their origins, behaviour and chemical structures. Gums submitted to a hydrolysis process, because of their polysaccharide nature, produce an indefinite number of monosaccharides. Depending on the type of the products obtained by hydrolysis, gums can be further classified into pentosans and hexosans. Chemically, they are pathological products consisting of calcium, potassium and magnesium salts of complex substances known as polyuronides, whose sugar units can be separated by hydrolysis using dilute mineral acids, followed by separation of liberated monosaccharides using different chromatographic techniques [3]. Different sources of gums and mucilages are listed in Table 1.

Plant-based gums are the polysaccharides originated from various parts of plant (e.g. plant cell walls, tree exudates, seeds, tuber/roots, seaweeds) [6]. Most of them belong to the Leguminosae family, which is divided into the subfamilies Caesalpinioideae, Mimosoideae and Faboideae [15]. The polysaccharides sourced from plants are examples of natural compounds that have contributed to the Leguminosae family classification, but special emphasis has been given to galactomannans [16].

The considerably growing interest in gums is due to their diverse structural properties and metabolic functions in food, pharmaceutical, cosmetic, textile and biomedical products [17], since they can be used as dietary fiber, texture modifiers, gelling agents, thickeners, emulsifiers, stabilizers, coating agents and packaging films [6,18]. In the recent years, the demand for plant-based gums in food, medicine and drug delivery systems have been considerably increased because they are the most notable ingredients in liquid and semisolid foods [19]. However, the market still desires new sources of plant-based gum to meet the demand for ingredients with more usefulness especially in food systems [6], hence they are the new generation of products sourced from sustainable materials that intend to comply the ecological and economic requirements.

Acting as soluble dietary fibres, gums play a crucial part in developing foods with high satiating capacity due to their viscosity. Most of the scientific researches mention that when gums are hydrated, they increase the viscosity of the solution medium and show a very wide range of rheological behaviour, generally pseudoplastic, depending on their concentration, chemical arrangement and structure [20].

Table 1. Classification of the different available gums and mucilages.

Source	Name	Type	Reference
Tree gum exudates	Arabic gum	Arabinogalactan	[21]
	<i>Prosopis alba</i> gum	Arabinogalactan	[22]
	<i>Acacia tortuosa</i> gum	Arabinogalactan	[23]
	Almond gum	Arabinogalactan	[24]
	<i>Albizia stipulata</i> gum	Arabinogalactan	[25]
	<i>Acacia senegal</i> gum	Arabinogalactan	[26]
	Cashew gum	Galactan with glucose, arabinose, rhamnose, mannose and glucuronic acid units	[27]
Extracts	Pectin	Galacturonic acid with rhamnose, arabinose, galactose, xylose, and glucose units	[28]
Seeds	<i>Cassia spectabilis</i> gum	Galactomannan	[29]
	Guar gum	Galactomannan	[30]
	<i>Cassia nodosa</i> gum	Galactomannan	[31]
	<i>Cassia grandis</i> gum	Galactomannan	[32]
	Fenugreek	Galactomannan	[33]
	Locust bean gum	Galactomannan	[34]
	Starch	Glucan	[35]
	<i>Hymenaea courbaril</i> gum	Xyloglucan	[36]
Red seaweeds	Agar	Galactan	[37]
	Carrageenans	Galactan	[38]
Brown seaweeds	Alginate	Mannuronic acid with guluronic acid units	[39]
Microbial	Xanthan gum	Glucan	[40]
	Cellulose	Glucan	[6]
Animal	Chitin	Glucosamine	[41]
	Hyaluronic acid	Glucosamine with glucuronic acid units	[42]
	Chondroitin sulphate	Galactosamine with glucuronic acid units	[43]

Studies dealing with gums as texture modifying agents are continuing to increase in the food and culinary industries, especially for gelling, thickening and emulsifying purposes. Some hydrocolloids are used as gelling agents, for example, to increase the satiety sensation in the stomach, brought about by different triggering factors. It is believed that, in order for gastric gelation to induce satiety, not only must a gel form in the stomach but the gel must also possess some strength [44]. Also as regards the food industry, the most common polysaccharides used for production of edible films are cellulose, chitosan, agar, starch, and no less important, galactomannans, since their mechanical and thermal properties have been widely exploited for biotechnological application.

Not only in food and culinary industry, but also in biomedical applications, the synergistic interactions that occur in systems containing different blends of polysaccharides have been used for a long time due to their ability to form strong gels even at low concentrations [45]. Still in view of the medical field, some of the current challenges in the conventional therapeutic systems include lack of proper drug delivery systems with efficient bioavailability or drug release capability, lack of efficient imaging and sensing technique, lack of targeted delivery systems, etc. As an attempt to circumvent these issues, the advent of nanotechnology allows the use nano-tools to overcome the shortcomings of the conventional methods [46], therefore, natural gums are being processed into various forms, including the most recent nanomaterials, for various biotechnological applications. The main natural polymers, including gums and mucilages, as well as the current researches about them are reviewed below.

3. Galactomannans

Galactomannans are neutral polysaccharides isolated from seeds. The main chain is composed of (1→4)- β -D-mannose (M) units with different degrees of substitution on O-6 with α -D-galactopyranosyl (G) units (Figure 1). Galactomannans are considered highly water soluble hydrocolloids providing highly viscous and stable aqueous solutions, in addition, its solubility depends on the composition (or M/G ratio) and on the distribution of galactose units along the mannan backbone chain: the larger the galactose content, the higher the solubility in water [47].

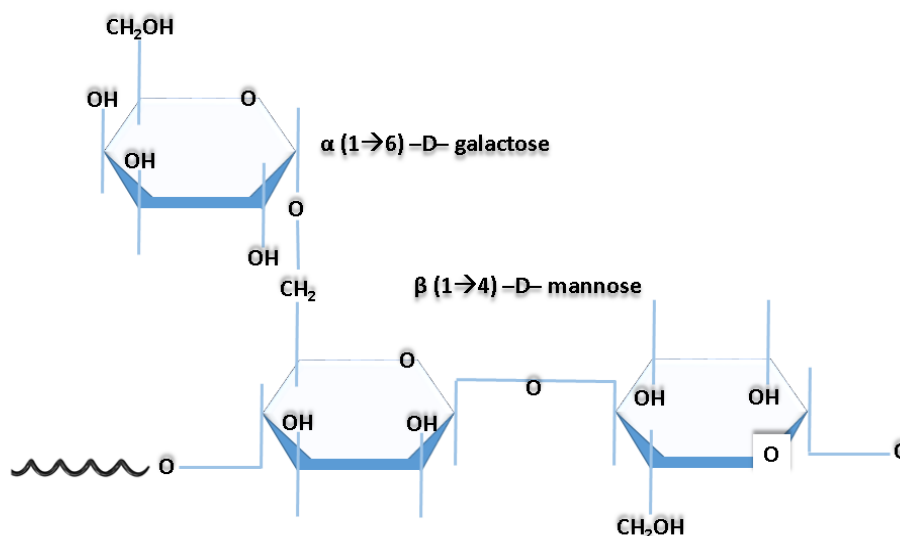


Figure 1. Representative segment of a galactomannan main chain from plant origin.

The M/G ratios varies among the species of the same subfamily. Caesalpinioideae presents M/G ratios ranging from 2.44 (*Cassia grandis*) [32] to 4.2 (*Delomix regia*) [48] and its main representatives are *Cassia tora* (M/G: 3.0) [49], *C. spinosa* (M/G: 2.7–3.0) [49,50] and *Ceratonia siliqua* (M/G: 3.5–3.75) [51]. Mimosoideae subfamily presents lower M/G ratios, usually varied from 1 (*Mimosa scabrella*) [52] to 2.6 (*Besmanthus illinoensis*) [49]. Faboideae subfamily presents a broad range of

M/G ratios for its representatives and includes the main commercially used galactomannan in food and non-food industries, the guar gum (*Cyamopsis tetragonolobus*, M/G: 1.8) [53].

Galactomannans are polysaccharide gums with several functions associated in terms of their physicochemical and biological properties, which in fact offer a wide variety of applications. Unlike other gums, galactomannans or their derivatives are less exploited on an industrial scale, despite milled endosperm powders of guar, locust bean (*Ceratonia siliqua*), and fenugreek (*Trigonella foenum-graecum*) represent the galactomannan seeds currently exploited on an industrial scale [54]. Among their applications, these gums accumulated moisture (desiccation tolerance) at the early stage of seed swelling and serve as a carbohydrate energy resource during seed germination. In addition, galactomannan gums may also play a protective role, since they impart certain strength to the endosperm surrounding the germ at the periphery [55].

Compared with other gums, galactomannans exhibited excellent retention of viscosity even at low concentrations. They can be used as mass-efficient aqueous thickeners, nutritional supplements [11,40], and component in a mixed gel [56,57]. In the food industry, galactomannans as guar and locust bean gum enjoy widespread use based on their ability to thicken and stabilize many food products [55]. More recently, some works reported the possibility of using galactomannans in the formation of films and coatings [14,59-61].

In some works, galactomannans have been used in binary mixtures with other polysaccharides such as xanthan gum [62-64], agar [65] and kappa carrageenan [58,66], to form gels with new properties. Among the oil and textile industries, galactomannan gums are the major ingredients in drilling mud and are used mainly also for their capacity to increase printing quality. The functional properties of these polysaccharides are of primary importance for controlling the release of drugs in the pharmaceutical industry [67,68].

4. Cellulose

Cellulose, the major structural constituent of the cell wall of plants, is the most abundant polysaccharide in nature. It has many advantages, such as superior thermal and mechanical properties, in addition to biocompatibility, biodegradability, and cost-effectiveness [69,70].

One of the most successful biomaterials for health is the bacterial cellulose, a promising biopolymer obtained through biosynthesis routes by some bacterial genera belonging to *Acetobacter*, *Rhizobium*, *Agrobacterium*, *Aerobacter*, *Achromobacter*, *Azotobacter*, *Salmonella*, *Escherichia*, and *Sarcina* genera. Bacterial cellulose has been extensively studied due to its purity, superior physico-mechanical and biological properties, as well as its potential applications in numerous traditional industries, such as biomedical, construction, pulp and papermaking, in addition to textile industry [71-73].

The biosynthesis of cellulose is a process commonly associated to the living plant cell through photosynthesis. In the oceans, however, most cellulose is produced by unicellular plankton or algae using the same type of carbon dioxide fixation found in photosynthesis of land plants. In addition, several animals, and microbial can assemble cellulose, but these organisms are devoid of photosynthetic capacity and usually require glucose or some organic substrate synthesized by a photosynthetic organism to assemble the polymer [74]. According to Nobles et al. [75], even most cellulose widespread in nature is now being produced by plant cellulose synthase complexes; this

enzyme has bacterial origin, therefore its genes have been acquired by plants from cyanobacterial ancestors of their chloroplasts.

Despite the most recent literature dealing with the elucidation of the molecular mechanisms of cellulose biosynthesis in plants, many aspects of this process still remain obscure. Especially for bacterial cellulose biosynthesis, the model system associated with the microbial origin of cellulose has long been used as a simpler and genetically tractable model to study its biosynthesis in plants. Even after this model system became dispensable, studies of bacterial cellulose biosynthesis proved to be extremely important, since bacterial cellulose has advantageous characteristics over comparable with plant cellulose, including high crystallinity degree, elasticity, durability and higher water-absorbance [76-78].

In summary, there are four main different pathways to obtain cellulose: the first is the most popular and industrially important pathway for isolating cellulose from plants, which includes the chemical pulping, separation, and purification processes to remove lignin and other polysaccharides (hemicelluloses). The second pathway consists in the biosynthesis of cellulose by different types of micro-organisms (unicellular algae, fungi, and bacteria). The third pathway is the enzymatic *in vitro* synthesis starting from materials such as cellobiosyl fluoride. The last pathway is a chemical synthesis, that produces cellulose through a ring-opening polymerization of the benzylated and pivaloylated derivatives of glucose [73].

In what concerns the basic structure of cellulose, it is a simple polysaccharide with no branching or substituents in its homogeneous backbone (Figure 2). The morphological hierarchy of cellulose is composed by elementary fibrils, which pack into larger units called microfibrils, and these are in turn assembled into fibres. Within the cellulose fibrils, there are regions where the cellulose chains are arranged in a highly ordered structure (crystallites) and regions that are disordered (amorphous-like). The extraction of the crystalline regions results in nanocrystalline cellulose (NCC), while the interaction between inter- and intra-molecular networks can vary, giving rise to cellulose polymorphs or allomorphs [79,80].

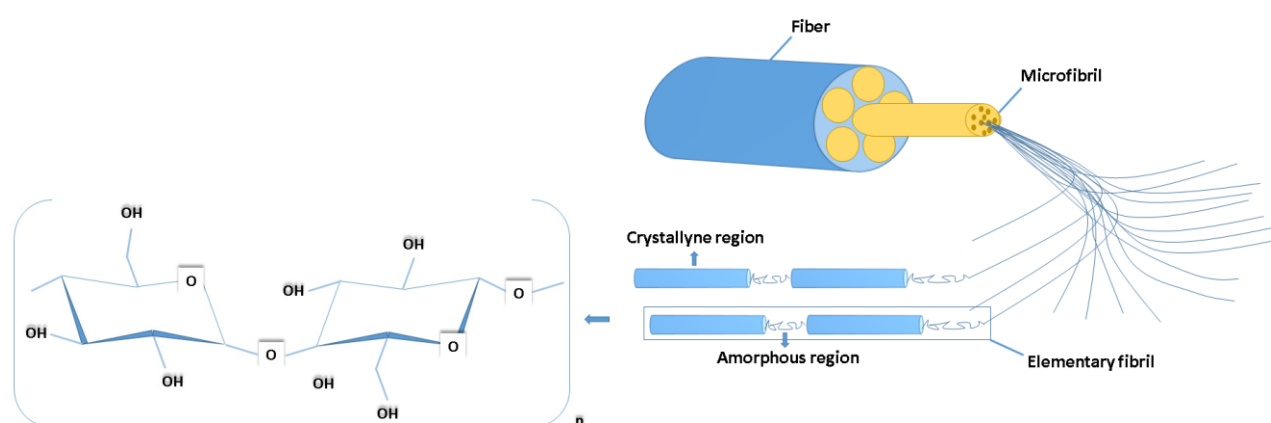


Figure 2. Representative image of the cellulose main chain and the hierarchical structure of this polysaccharide.

NCC is the base reinforcement unit that strengthen all subsequent structures in plant, trees, etc., and can be a useful material on which to base a new polymer composite industry. NCC has also properties such as low density, high specific strength and modulus, high surface area, unique optical properties, and modifiable surface properties due to the reactive hydroxyl groups [81]. Advantages in

the biotechnological application of NCC when compared to macrocellulose are related not only to their useful, unsurpassed, physical and chemical properties, or to their sustainability, biodegradability, renewability, abundance, high biocompatibility. Actually, the nanoscale dimension opens a wide range of possible properties to be discovered. According to Fujisawa et al. [82], NCC can be divided in three major groups: (1) cellulose nanocrystals (CNC), obtained from acid hydrolysis followed by mechanical agitation from the suspension of nanocrystals in water; (2) microfibrillated cellulose (MFC), prepared with mechanical disintegration method of the cellulosic pulp in water; and (3) nanofibrillated cellulose (NFC), prepared using a combination of chemical oxidation with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), followed by mechanical disintegration in water, or only by mechanical disintegration.

It is important to highlight that the hydroxyl groups are the most targeted reactive groups on the cellulose main chain; they can fully or partially react with chemical agents to obtain various derivatives with different degree of substitution. For upgrading the value of cellulose, the obtained derivatives have been developed and used in industries such as food, cosmetic, biomedical, and pharmaceutical. However, the application of cellulosic material is limited due to the difficulty in processing, for example, the high crystallinity degree and rigid intra/intermolecular hydrogen bonds which result in its insolubility in most solvents [35,83].

The above mentioned problems associated with the processing of cellulose could be observed for other natural polymers since they present increasingly application in the industrial technology. In addition, most polymers do not show biological activity unless some modifications are carried out, so it is important to mention that numerous attempts are being performed to minimize these certain drawbacks with chemical modifications in the polymeric structure.

The most important chemical transformation and functionalization of cellulose based on hydroxyl group include esterification, etherification, selective oxidation, graft copolymerization, and intermolecular crosslinking reaction [84]. The esterification process of cellulose was applied for different purposes, such as the preparation of superabsorbent hydrogels [85] and bacterial cellulose nanofibers [86]. The etherification process of cellulose was especially applied in the pharmaceutical industry, for example to obtain NFC as safe candidate for novel, bio based, and permanently antimicrobial material [87]. The oxidation of primary hydroxyl groups of cellulose is one of the most important methods of their functionalization, which yields valuable oxidized products such as polyuronic acids and aldehydes, to be further used in various fields as drugs, dyes, glues, thickeners, additives to foodstuffs, cosmetics and many other. Oxidized cellulose and regenerated cellulose are widely used as excellent hemostatic materials in various surgical operations and postsurgical adhesion prevention layer [88-90].

Regenerated cellulose has also been used as films; cellophane films, for example, have not been commonly used for food packaging, due to their high water vapour permeability (low barrier properties) compared to their synthetic counterparts. On the other hand, transparent cellulose films exhibit good oxygen and CO₂ barrier properties at dry conditions. They are made from purified wood or cotton pulp sheets and have important characteristics such as transparency, durability, flexibility, non-water solubility and non-permeability to air and grease. Other transparent cellulose films such as MFC and NFC film have emerged as a potential packaging material due to their strong mechanical properties [91,92].

Currently, there are two oxidation systems to selectively convert the primary hydroxyl groups in cellulose into carboxyl and/or aldehyde groups: (1) 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and its derivatives; (2) N-hydroxyphthalimide (NHPI), N-hydroxy-benzotriazole (HBT), and violuric

acid (VA) [93,94]. The amount of carboxylic groups formed by oxidation of cellulose was investigated for different and important purposes, such as the following examples. A comparative investigation between TEMPO and NHPI to oxidize regenerated cellulose fibers [95], the potential of TEMPO-mediated oxidized NFC as bioremediator of metal ions from contaminated water [96]; the *in vitro* antibacterial evaluation of TEMPO-oxidized cellulose films functionalized with silver nanoparticles [97]; and the preparation of water stable films made of TEMPO/NaClO₂ oxidized NFC, covalently bonded with poly(vinyl alcohol) [98].

Another approach for cellulose modification via chemical redox initiation methods (ceric ammonium nitrate or ferrous ammonium sulphate–potassium persulfate) or irradiation methods (UV, microwave, and γ -rays) is the graft copolymerization, which provides a mean of altering the physical and chemical properties of cellulose and increasing its functionality [35,97-101].

Nowadays, the research on cellulose nanocomposites has grown exponentially. As definition, cellulose nanocomposites are structures composed of water-soluble or water-dispersive polymers mixed with cellulose nanomaterials, and manufactured using different processes able to affect properties such as dispersion, distribution and alignment of the reinforcing phase of the composite [102]. The most recent literature dealing with cellulose nanocomposites described the employment of the microwave-assisted method on the investigation of the influence of cellulose on nanocomposites of cellulose/Ag [103], cellulose Ag/Cl [104], cellulose/SrF₂ [105], cellulose/CaF₂ and cellulose/MgF₂ [106], and cellulose/F-substituted hydroxyapatite [107]. The pharmaceutical field has important studies, for example, all cellulose nanocomposite membranes with excellent performance were successfully fabricated as novel filtration system to remove nanoparticles and Hepatite C virus from aqueous medium [108]. Transparent porous nanodiamonds/cellulose nanocomposite membranes with controlled release of doxorubicin were tested as a candidate for wound dressing [109]; and cellulose-graft-polyacrylamide/nano-hydroxyapatite composites were reported as a promising scaffold for bone tissue engineering [110,111].

5. Polysaccharides from animal origin

Glycosaminoglycans (GAGs) are heteropolysaccharides composed by a repeating disaccharide unit without branched chains, being one of the two monosaccharides always an amino sugar (N-acetylgalactosamine or N-acetylglucosamine) and the other one an uronic acid. They are usually found on all animal cell surfaces and in the extracellular matrix, where are known to bind and regulate different proteins. In the last years, an increasing number of GAGs, chitin and chitosan applications have been reported by the scientific literature reporting their applicability in numerous contexts from food, cosmetic, textiles and clinical areas [43].

Chondroitin sulphate (CS) is an essential component of extracellular matrix of connective tissues in which plays a central role in various biological processes, including the elasticity of the articular cartilage, hemostasis and inflammation, regulation of cell development, cell adhesion, proliferation and differentiation [43]. Hyaluronic acid (HA) is classified as a viscous substance with multifunctional properties, especially those related to biological functions like cell proliferation, differentiation and tissue repair; the applicability of HA has been focused recently as drug delivery devices with studies suggesting a number of molecules might be used as gel preparations for drug transport. Since the application of the polysaccharide in the medicinal field has been increased, the interest in isolation of HA has been augmented to greater extents [112].

Although CS and HA has been isolated from terrestrial origin so far, the increasing interest on these polysaccharides significantly aroused the alternative search from marine sources since it is at the preliminary level. However, chitin is still the main waste product of the shellfish industry and, due of this importance, will be detailed revised below.

Chitin

Chitin is the second most abundant polymer after cellulose [89]. Its chemical structure (poly- β -(1 \rightarrow 4)-*N*-acetyl-D-glucosamine) is widely synthesized in a number of living organisms, which depending on its source, chitin occurs mainly as two allomorphs, namely α (the most abundant) and β forms [47]. Sharing the classification of natural polymers from animal origin with CS and HA, chitin can be found in many organisms including fungi, yeasts, algae and squid pen; it is also usually found in lobsters, crab tendons, shrimp and crab shells as well as insect cuticles, being shells the preferred source of chitin due to their high availability as waste from the seafood processing industry [43,47].

Chitin occurs in nature as ordered crystalline microfibrils found as structural components in the cell wall of fungi and yeast or in the exoskeleton of arthropods. The main commercial sources of chitin are crab and shrimp shells, where chitin is associated with proteins, pigments and calcium carbonate. The physical properties of chitin in solution are still scarce in the literature due to the difficulties in dissolving the polymer; chitin is insoluble in all usual solvents, which represents a problem in view of the development of processing and of its uses [47].

Chitin can be partially degraded by acid to obtain a series of oligomers namely oligochitins. Instead, under alkaline conditions, a partial deacetylation of chitin results in the most important chitin derivative in terms of applications: chitosan (Figure 3). Oligochitins as well as those from chitosan are recognized for their bioactivity including antitumoral [113,114], antimicrobial [115], fungicidal [116] and immunotherapeutic [117] properties, eliciting chitinase [118], and regulating organism growth [111].

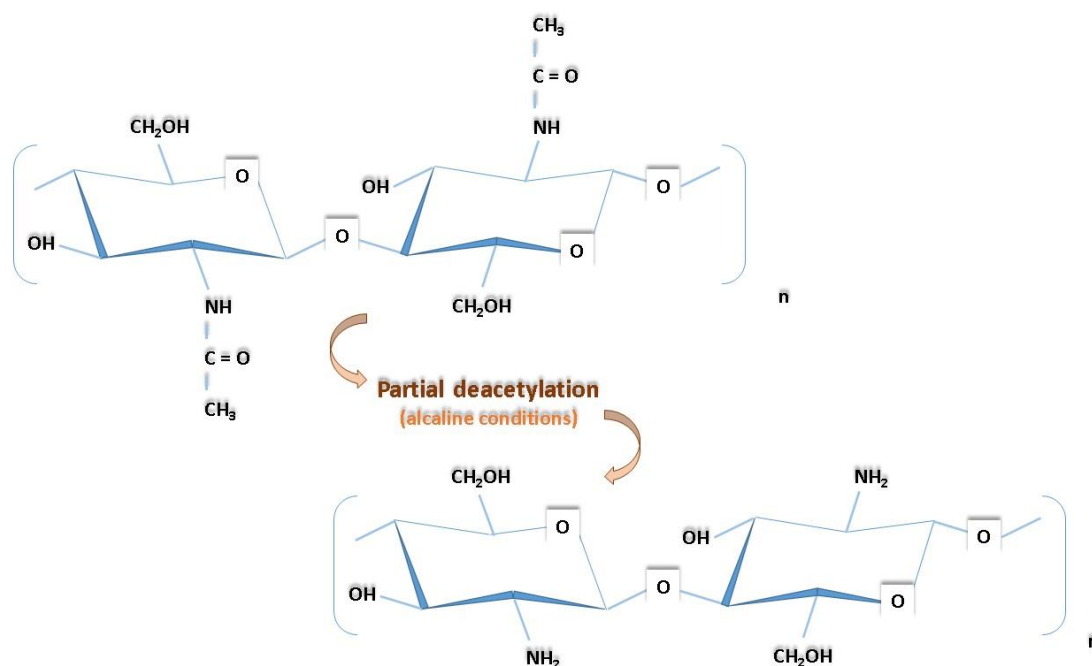


Figure 3. Representation of chitin and chitosan structures. “n” is the degree of polymerization.

Chitin is an amino polysaccharide having massive structural propensities to produce bioactive materials with innovative properties, functions and a range of biotechnological applications. In addition, the specific physicochemical, mechanical, biological and degradation properties offer efficient way to blend this biopolymer with synthetic ones [119].

Chitin has a low toxicity and it is inert in the gastrointestinal tract of mammals. Chitinases and lysozyme from egg white can degrade chitin; in the first case, the enzymes are widely distributed in nature, found in bacteria, fungi and plants as well as in the digestive tract of numerous animals. After the deacetylation process, it was shown that the rate of in vivo degradation is high for chitin, but decreases for chitosan [47,120].

The main applications of chitin are in medical and pharmaceutical fields, especially due to the presence of the acetamide group, which is similar to the amide bond of the protein of the living tissue and, therefore, is compatible with human or animal cells. Hence, chitin can be used in wound healing [121,122] and tissue engineering applications [123,124].

Still in view of wound dressing materials, Morgado et al. [125] remarked that chitosan had also been used for wound dressing production due to its intrinsic properties, including antimicrobial and hemostatic activities, biocompatibility, and biodegradability. Chen et al. [126] and Lih et al. [127] also highlighted the potential application of chitosan as wound dressing due to the recognition of its surface by platelets. The coagulation cascade starts in a few seconds with the protonated amine groups of chitosan attracting the negatively charged residues on red blood cell membranes, resulting on a strong agglutination, thrombin generation and fibrin mesh synthesis within the microenvironment created by this polysaccharide.

The marked insolubility of chitin in all usual solvents is the most different property compared to chitosan, which is the only commercially available water-soluble cationic polymer due to the positive charges on its amino groups. The water solubility of chitosan allows the interaction of this cationic biopolymer with anionic molecules such as glycosaminoglycans (GAG) and proteoglycans. Many cytokines/growth factors are linked to GAG, so the complex of chitosan-GAG may retain and concentrate those substances [128]. This unique property makes chitosan an appropriate material not only in the biomedical and pharmaceutical fields; instead, the antimicrobial and gas barrier properties of chitosan were successfully applied in the food industry, for example, in a nanomultilayer coating obtained by electrostatic layer-by-layer self-assembling technique; by combining the intrinsic properties of chitosan and the low oxygen permeability of pectin, layers were efficient in the reduction of gas flow and on the extension of the shelf-life of mangoes [129]. Chitosan-based films with quercetin incorporated also showed potential to be used as a solution for active food packaging [130]. The positive charge of chitosan was also used in the development of a high-efficient gene delivery formulation combined with polyethylenimine and DNA by Min et al. [131], who achieved a system less cytotoxic than those made of a single cationic carrier.

Many applications were described based on chitin and its blends for tissue engineering, for example, Wan and Tai [132] presented a revision of chitin as scaffolds and matrices for tissue engineering, stem cell propagation and differentiation. Polymer matrix–calcium based composites were used for hard tissue substitutes [133], in addition to drug delivery [134]. Chitin is also efficient to give porous forms providing scaffolds for complete tissue formation [135,136].

In what concerns drug delivery system, chitin and its derivative amorphous chitin, alone or with other polymers, have been widely used due to its biocompatible, biodegradable and non-toxic nature [137]. Further, more recently application takes into consideration the high surface area presented in nanometric

systems, especially because of the nano-size possess certain unique properties which enable them to be used in a number of biomedical applications. Prepared by cross-linking reaction using TPP, chitin nanoparticles were described as efficient networks for drugs with antitumoral [138,139] and antibacterial [137] purposes. Working with one derivative of chitin containing carboxyl groups (CMC), Dev et al. [140] have taken the approach of cross-linking the CMC as a way to control its biodegradability and to result in nanoparticles, providing a most favorable option for drug delivery applications in chemotherapy. Chitin nanoparticles can be also isolated from the purified chitin by repeated acid hydrolysis and applied for different purposes, such as the development of bio-nanocomposites with starch [141] and as a suitable adsorbent material for the removal of dyestuff from effluents [142].

Chitin can be used in the food industry because of its biological activities including antioxidant and antimicrobial effects. In addition to other properties that could improve food safety, quality, and shelf life [143], however the main publications dealing with protective barrier against food spoilage [144,145], edible film production [146-150], use as stabilizers and thickeners compounds [143], and prebiotics ingredients [151] related chitosan as the most efficient biomaterial in this field.

6. Seaweed polysaccharides

Algae are an important source of many polysaccharides from the point of view of applications, in addition to be the oldest known living organisms. Morphologically, they are very primitive and their evolution was very slow over time. Blue-green algae (Cyanophyta) appeared first, followed by red algae (Rhodophyta), green algae (Chlorophyta) and finally brown algae (Phaeophyta). Algae are in fact rich in non-essential and essential amino acids such as proline, glycine and lysine, besides many other molecules [39,47].

It was recognized that the three main gums, agar, alginate, and carrageenan, could be extracted from algae and used especially as thickeners or gelling polymers. Their physical properties are efficiently used in food, however new applications of algae are being developed, for example in the production of drugs and pharmaceuticals. Red seaweeds contain agar (mainly neutral), carrageenans and a few other polysaccharides included under the category of sulphated polysaccharides. Brown algae produce alginates, a carboxylic polymer, initially in different ionic forms and a few other polysaccharides, among them fucoidans [47].

6.1. Agar and carrageenan

Algae derived from Rhodophyta are an important source of polysaccharides, which are sulphated glycans together with a variety of *O*-methylated sugar residues, among them carrageenans and agars, polysaccharides commonly used in industry. The basic structure of these polymers is composed of a linear chain of β -D-(1 \rightarrow 3) galactopyranose and α -D/L-(1 \rightarrow 4) galactopyranose units (Figure 4) arranged in an alternating sequence [47].

Polysaccharides sourced from red algae have attracted an increasing interest due to their excellent physical properties, such as thickening, gelling, and stabilizing ability [152,153], and also due to their beneficial biological activities, such as anticoagulant [154], antithrombotic [38], antioxidant [155], antiviral [156,157], anti-inflammation [158], antitumour [159], and immunomodulatory activity [160]. It is important to highlight that their biological activities depend on the structural features, such as the sulphate content and distribution of sulphate groups on the main chain, molar mass, and stereo-chemistry.

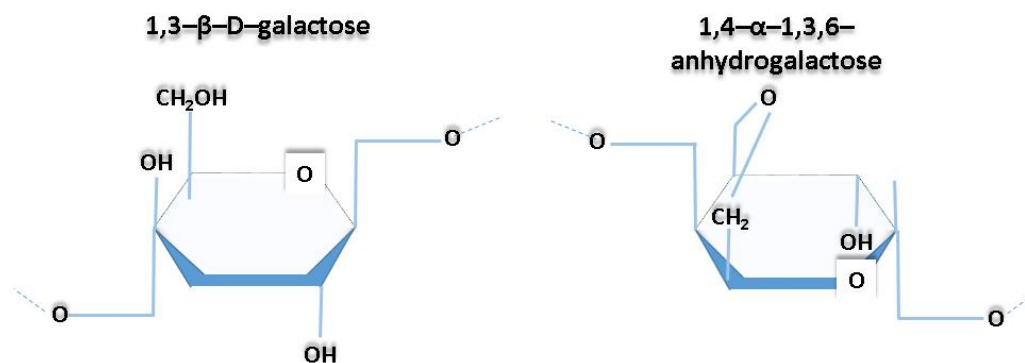


Figure 4. Chemical structure of repeat units of polysaccharides sourced from red algae.

6.1.1. Agar/agarose

Agar is a gelatinous substance composed of alternating D- and L- galactopyranose units. Its macromolecular structure consists in a mixture of agarose and agarpectin. Agarose is the neutral fraction of agar, and it is obtained by precipitation of the anionic agaropeptins by quaternary ammonium salt and separation by centrifugation. Agaropeptin is a heterogeneous mixture of smaller molecules, which have similar structures with agarose but contains many anionic groups such as sulphate, pyruvate and glycuronate. Due to the similar chemical and physical properties with agarose, agar has also been widely studied and applied in the biomedical field because of its good biocompatibility, biodegradability, nontoxicity, availability and lowcost [47,161].

Agarose adopts a single or double helical conformation in the solid state. Gelation occurs by aggregation of double helices at a temperature dependent on methoxyl and sulphate contents, which can modulate this process. The three-dimensional network based on association of double helices is thermoreversible, i.e., the crosslinks occur physically without chemical catalyst or any crosslinking agent, and it is stabilized by cooperative hydrogen bonds. Therefore, the low cost, special mechanical properties, biocompatibility and relatively bioinert nature make agarose a promising alternative as a gel matrix [47,162].

Since agar and agarose have good biocompatibility and excellent moisturizing capacity, many applications were described in the literature. Various forms of systems based on agar and agarose have been developed for the applications in pharmaceutical industries and medical research: Miguel et al. [163] produced a new *in situ* thermo responsive hydrogel composed by agarose and chitosan to be used as an injectable scaffold for tissue regeneration. They corroborated Varoni et al. [164], who described agarose hydrogels as mouldable materials, i.e., the hydrogel may be polymerized *in situ* reducing invasiveness of the surgery, besides it also be able to acquire the right shape at the wound site, without wrinkling or fluting and interacting with the damaged tissue. Agar and agarose fibers were fabricated by Bao et al. [161] and demonstrated to be good candidate materials for wound-dressing applications.

The scientific literature reported that the use of hydrogel as biomaterials for wound healing is also promising, however, they usually exhibit relatively poor mechanical properties due to the high swelling ratio, which limits their practical applications as wound dressings. Therefore, the most recent studies demonstrated that the incorporation of nanomaterials is probably the effective strategy to improve the mechanical property of hydrogels [165]. Wang et al. [166], for example, developed

nanocomposite hydrogels based on agarose and ZnO and concluded that the system might be an excellent candidate for wound dressings.

Agarose can be processed by extrusion from solution at high temperature, forming gel beads into ice-cold buffer. Another method is to emulsify agarose in a warm fluid which is immiscible with the aqueous polysaccharide solution; the emulsion is then cooled and produce microspheres [167]. Large-sized agarose beads can be prepared by some typical techniques, such as mechanical stirring and spraying methods. However, these methods suffer from poor control of droplet size and size distribution, low energy efficiency, and time consuming characteristics. Li et al. [168] improved the emulsification reproducibility and stable bead properties by developing a manufacturing protocol for uniform droplets and beads of controlled size with rotating membrane emulsification.

Agarose is also widely used as growth medium for microorganisms (bacteria and fungi) [169-171] and for biotechnological applications. Agarose was submitted to an enzymatic hydrolysis process with no acid treatment and converted in a potential hydrolysate for bioethanol production [172]. By casting and subsequent drying process, agar and agarose films can be formed depending on the application [173,174].

In the food industry, it is well known that agar films possess several properties adequate for food packaging applications, however, their high cost-production and quality variations caused by physiological and environmental factors affecting wild seaweeds make them less attractive for industries [175]. Despite having good mechanical and relatively good oxygen and water barriers properties, the most recent trends in food industry use nanomaterials as promising option to improve mechanical and barrier properties of biodegradable agar-based composite films [176-178].

In the domain of blends, agar was mixed with different materials, for example, poly(vinyl alcohol) and soy protein, respectively for specific food applications [179] and for scanning the variations in the matrix tensile strength [180]. Agar and agarose were also mixed with different polysaccharides to produce blends with potential biotechnological applications. Agarose was mixed with fenugreek galactomannan and formed a matrix efficiently used as biosensor to detect pesticides in food [181]. Multicomponent hydrogel films composed of agar, κ -carrageenan, konjac glucomannan powder, and nanoclay improved mechanical and water resistant properties of the blended hydrogel film [182]. Recently, agarose blends have been used in nanotechnological process, such as the rheological study of agarose hydrogels with tunicate cellulose nanowhiskers [183].

6.1.2. Carrageenan

Carrageenan is a word that seems to originate from the inhabitants of the country of Carrageen, on the south Irish coast where extracts from red algae for food and medicines were already used as early as 600 years ago. The major constituent of such algae is the so-called carrageenans, naturally occurring anionic sulphated linear polysaccharides with the linear backbone built up by β -D-galactose and 3,6-anhydro- α -D-galactose with variable density in the sulphated group [38,184].

There are several different carrageenans with slightly varied properties and chemical structures. The three most prevalent and of highest commercial interest are called iota, kappa, and lambda carrageenan, differentiated based on the amount and position of sulphate groups, and serving different properties [38].

Carrageenans have been extensively used in the food industry as thickening, gelling, stabilizing and protein-suspending agents due to its biocompatibility, biodegradability, high capacity of water retention and mechanical strength of its gels. According to the properties of carrageenan, it can split into two groups like, gelling (kappa and iota) and thickening agent (lambda); the 3,6-anhydro- α -D-galactose

is essential for the gelling properties of kappa and iota carrageenans. The molecular weight of carrageenans is critically important to its functionality in food, so, as stabilizers, carrageenans achieve its functionality due to its high molecular weight and binding capacity to proteins through charged sulphate and carboxyl groups [185].

The most recent applications of carrageenans are described in the following. Encapsulation of β -galactosidase in kappa carrageenan hydrogel beads was investigated for the application in food industry [186]. Multilayer coatings composed of kappa carrageenan and chitosan were produced, characterized in terms of their permeability's and surface properties [187], and used as model for the release behavior of Methylene blue; the industrial relevance of this type of nanolayered coatings consists in the development of bioactive compound release systems for application in food industry [188]. Multilayer films with a nanocomposition of kappa carrageenan, agar, clay and polylactide were prepared to modify the mechanical and barrier properties of the film for the food packaging application [189]. Still in view of the nanoscience, carrageenans were used not only as carriers of active antimicrobial nanoparticles, but also as polymer matrices for biodegradable films, for example, nanocomposite films with carrageenan, silver nanoparticles and clay mineral were prepared to test their combined effect on the antimicrobial activity and physicochemical film properties [190].

The biological activity of carrageenan as a natural occurring gum has been increasing widely for human applications and creates a strong position in the biomedical field [38], but it is important to highlight that the preliminary studies reported carrageenans administered in drinking water or diet could be a potential cause of intestinal inflammation and ulcers in animals [38,191]. Later, it was determined that these studies and others were conducted with a different material obtained by a degradation of the carrageenan that resulted in a sulfated polysaccharide with the same structural backbone to carrageenan, but with a lower molecular weight and different functional properties. Degraded carrageenan is referred to as poligeenan [185,192], polymer obtained by acid hydrolysis at high temperatures for several hours [185,193]. Poligeenan is also used in food applications, however, it was related to capable of causing gastrointestinal irritation in experimental animals and was considered to cause gastrointestinal cancer in animals. Carrageenans do not cause these effects and is safe at maximally administered oral doses [185]; they are related to inflammation just as employed in laboratories to create pathological models for exploration of the process and treatment of the inflammation [194-198].

Regarding the biological activities of carrageenans, its effect as food supplement was investigated on the immunity status and lipid profile in patients with cardiovascular disease. The results demonstrated that carrageenan moderately modulated all of the immunity system markers, caused statistically significant decreases in important biomarkers of chronic inflammation and significantly decreased cholesterol levels and low density lipoprotein cholesterol [199]. Besides the well-known biological activities related to inflammatory, immune [200], antioxidant [201-203], and antitumor responses [204,205], carrageenans are potent inhibitors of herpes and HPV viruses and there are indications that these polysaccharides may offer some protection against HIV infection [38,200].

Anticoagulant activity could be the most attractive property associated to carrageenans [154,160,206] and also to other sulphated polysaccharides, which were reported to possess similar or even stronger activity than those of heparin.

Carrageenans have been used by the pharmaceutical industry as excipient in different forms of presentation. Hydrogels of kappa carrageenan containing CaCO_3 and NaHCO_3 were tested as pore forming agents by Selvakumaran and Muhamad [207], and the system with CaCO_3 was considered an

efficient floating drug delivery system for amoxicillin trihydrate. Iota-carrageenan was investigated not only as a drug-loaded polymer but also as an ionic polymer to increase the solubility of the lappaconitine analgesic-alkaloid [208]. Hydrogels composed of kappa carrageenan and synthetic or natural polymers were reported, such as the blend constituted of kappa carrageenan and polythiophene for the electrically controlled drug release of acetylsalicylic acid [209]. Carrageenans were also used by the Interpenetrating Polymer Network (IPN) technique, which possess several advantages like high swelling capacity and tremendous mechanical strength on the targeted and controlled drug delivery. For example, IPN beads of kappa carrageenan and sodium carboxymethyl cellulose using AlCl_3 as a crosslinking agent were evaluated on the drug release behavior of ibuprofen [210].

6.2. Alginate

Alginate is the most important polysaccharide derived from brown algae (Phaeophyta), and it can be also produced by soil bacteria (*Azotobacter vinelandii* and *Pseudomonas* species). This gum is composed of 1,4-linked β -D-mannuronic acid (M) with $4C_1$ ring conformation and α -L-guluronic acid (G) with $1C_4$ conformation, both in the pyranosic conformation and present in varying amounts. It was demonstrated that the physical properties in aqueous medium for these polymers depend not only on the M/G ratio, but also on the distribution of M and G units along the chain. In addition, the stiffness of the alginate chains as well as calcium complex formation could be attributed to the composition (M/G ratio) and distribution of M and G units in the chains [47].

The main property of alginates is their ability to retain water, in addition to gelling and stabilizing properties. Because of their linear structure, and high molecular weight, alginates form strong films and good fibres in the solid state. Gel formation is a very important characteristic for alginates; the higher content of G units form stable crosslinked junctions with divalent counterions (for example, Ca, Ba, and Sr, unless Mg), so the crosslinked network can be considered a gel (Figure 5). In addition, the low pH also forms acidic gels stabilized by hydrogen bonds [47].

As an anionic polymer, alginate forms electrostatic complex when mixed with a cationic polymer. The stability of the formed complex depends on the pH and salt concentration, but even in the best conditions, the complex is insoluble and thus allows the formation of fibres, films, and capsules. Many applications are proposed to these complexes, especially for the most investigated polyelectrolyte complex based on alginate and chitosan. For example, a nanomultilayer coating composed of sodium alginate and chitosan, obtained by electrostatic layer-by-layer self-assembling, onto aminolyzed/charged PET was characterized and presented highly functional properties and promising future for industrial applications [211]. This alginate-chitosan nanomultilayer coating was applied in fresh-cut mangoes and improved the microbiological and physicochemical quality, extending the quality and shelf life of fresh-cut mangoes up to 8 days [130]. The deposition of functionalized particles on multilayers based on chitosan-alginate was investigated with the aim to use the complex in opto-electronics, biosensors or medical applications [212]. Belscak-Cvitanovic [213] prepared chitosan-alginate beads to encapsulate and retard the release of caffeine in water. Wang et al. [214] developed chitosan-alginate coatings to deliver titanium substrates via electrodeposition and suggested the potential application of this composite coating in tissue engineering scaffolds field. One more example is the study of Seth et al. [215], who designed magnetic chitosan-alginate core-shell beads for oral administration of low permeable drug.

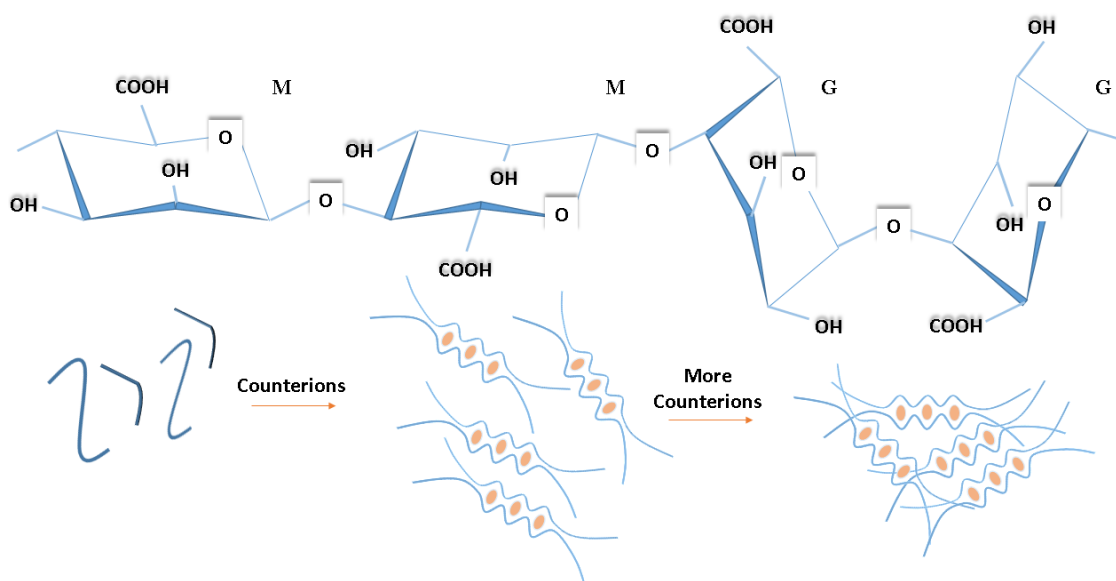


Figure 5. Chemical structure of repeated units of alginate: β -D-mannuronic acid (M) and α -L-guluronic acid (G), and the schematic crosslink between alginate and the counterions.

Several studies have shown that the chitosan-alginate complex acts as an effective way to improve the stability of encapsulated compounds [216,217]. It is important to highlight that, nowadays, the most extensively investigated delivery systems to encapsulate, protect and control the release of functional and unstable compounds in industries varying from food to pharmaceuticals consider the development of capsules in micro and nano scales. Liu et al. [218] optimized a formula of chitosan-alginate deposited nanoliposomes and observed an improved *in vitro* digestion stability. Haidar et al. [219] developed core-shell hybrid nanoparticles based on the layer-by-layer assembly of alginate and chitosan on liposomes and demonstrated that the polymer shell could increase the membrane stability and sustain release of the model protein. Liu et al. [220] evaluated the environmental stress stability of microencapsules based on vitamin C liposomes decorated with chitosan-alginate membranes and observed the release kinetics of these formulations during *in vitro* gastrointestinal digestion. Chitosan-alginate complexes loaded with other nano compounds were tested with different purposes, including bactericidal activity [221], tissue engineering [222], and osteochondral [223] and food [224] applications.

Other polyelectrolytes may also be involved to form complexes with chitosan-alginate, such as collagen [225], gelatin [226], inulin [227], BSA protein [228], poly(L-lysine) [229], poly(L-lactide) [230], and hydroxyapatite [231].

Regarding the characteristic advantages of alginates, including biocompatibility, biodegradability, immunogenicity, and gel formation, alginates are well adapted for biomedical and pharmaceutical applications, such as tissue engineering, delivery vehicles for drugs and cell or enzyme entrapment. In addition, alginates have been successfully used in the food industry, for example, to prolong shelf life of the products and protect bioactive compounds encapsulated in the alginate matrix [232,233]; they can also be used as an antioxidant active interface for food preservation [234], and as a part of matrices designed to improve the oxidative stability during food storage [235].

Taking into account the above mentioned characteristics of alginates, nearly all of them are harvested in their wild state; cultivation is too expensive to provide alginates at a reasonable price for industrial applications. The quantity and quality of the alginates extracted depend on the algae species and on the season of harvest; furthermore, the higher content of alginate is still directed to the food industry.

7. Gum extracted from *Anacardium occidentale*

Cashew gum (CG) is an exudate extracted from *Anacardium occidentale*, a popular tree belonging to the family Anacardiaceae. The cashew tree can grow up to 12 feet tall and is native to northeastern Brazil, however it can also be found in India, Mozambique, Tanzania, Kenya and among other countries. As a polysaccharide exudate, this gum is produced as a mechanism of plant defense against stress caused by physical injury or microbial attack. Its production can occur in all parts of the tree and its qualitative and quantitative depends on tree maturity and environmental conditions; initially, the gum is off white in colour but changes to reddish brown or yellowish brown on exposure. It is sparingly soluble in water but swells in contact with it giving a highly viscous solution [236-238].

The polyuronide CG is composed of a branched framework of D-galactose units. In addition, present are D-glucuronic acid, L-arabinose, L-rhamnose and, except in the case of a Venezuelan sample, D-glucose. D-xylose, D-mannose and 4-O-methyl-D-glucuronic acid have been found in some samples [239,240]. As a mixture of acid polysaccharides, CG contains various metal ions such as neutralized cations. The nature and content of these constituents depend on the composition of the soil upon which the trees grew. The major cations of *A. occidentale* are K^+ , Na^+ , Ca^{2+} and Mg^{2+} . Crude CG, containing these cations, tends to be naturally transformed into Na^+ salt, after purification or dialysis against $NaCl$ 0.15 M, as previously described [237,239]. Figure 6 demonstrates the chemical composition of the galactose framework of CG and a graphic representation of the sugars and cations possibly associated to the polysaccharide.

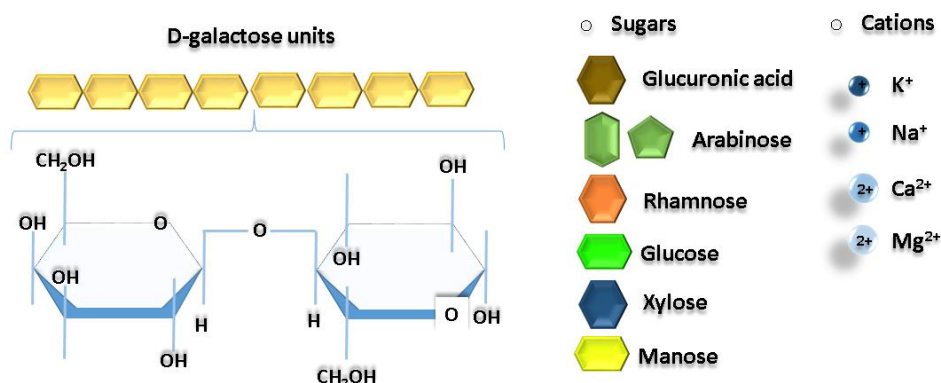


Figure 6. Representative image of the galactose main chain and possible sugars and counterions associated to the chemical structure of CG.

CG, as a versatile, naturally occurring biopolymer, is finding increasing applications in biotechnology industries, especially from pharmaceutical to food industry; however, there is a lack of understanding of its physicochemical properties thus limiting its applications. Chemical structure,

solubility and molecular weight of CG closely affect its solution properties as well as its interactions with other polysaccharides [239].

Modifications of gums have been tried through derivatisation of functional groups, grafting with polymers, cross-linking with ions, etc. The modification of CG can improve its technological and functional properties, since its application is related to a better understand on the physicochemical properties of the gum, in its original state or chemically modified, either isolated or blended with other polymer [241].

The unique properties of CG are due to hydroxyls, the majority, and to carboxyl reactive groups. This polysaccharide is easily chemically modified to reduce the water solubility or to develop pH sensitivity, introduce functional reactive groups, etc. Therefore, it can be utilised for a chosen application [237]. Thus, as the composition and properties of CG were disclosed, the chemical modification observed for blends composed of CG and other polymers were proposed to increase their reactivity. Following the use of CG blended with other polymers, the most recent literature reports the development of systems for drug release, like microbeads [242] and nanoparticles [243] of CG and alginate, and nanogels of CG and chitosan [244].

Several applications of blended CG were described, such as the production of films prepared with CG and polyvinyl alcohol (PVA) with the important purpose of wound therapeutics [245,246]. A layer-by-layer film containing CG intercalated with polyaniline unmodified or modified with phosphonic acid intercalated with CG was evaluated in determination of dopamine [247], and nanocomposite films of starch and CG were added to a nanoclay to increase the stability of cashew nut kernels [248]. Hydrogels based on CG (namely Policaju in this study) and chitosan were developed, characterized in their chemical structure, and indicated as a promising road to biomaterial fabrication and biomedical applications [249]. The larvicide activity of an essential oil loaded in beads based on chitosan and CG was evaluated by Paula et al. [250]; afterward, CG nanoparticles added with other essential oil was proposed to improve the controlled release of a larvicide system [251]. CG and carboxymethylcellulose based formulations have been evaluated as protective edible coatings on intact and cut red guavas [252].

The properties of CG have also been exploited as a binder, for example the binding efficacy of CG based on tablet formulation was investigated in comparison with standard binders such as acacia and polyvinyl pyrrolidone; the results suggested that CG can be used as an alternative binder to produce a tablet of better mechanical strength and dissolution profile of particular drug substance [253]. In addition, CG can be used as a substitute for liquid glue for paper, in the cosmetic industry, as an agglutinant for capsules and pills [237], and as edible coatings for application on mangoes [27] and apples [254].

Fabrication of systems utilizing CG for drug delivery have been an area of great interest, such as the transdermal release profile for diclofenac diethyl amine loaded with nanoparticles of acetylated CG [255]. Other example is the study about the controlled delivery of antimicrobial peptides immobilized in multilayer films of CG and indium tin oxide to combat and prevent anti-leishmanial activity [256]. Self-assembled nanoparticles from hydrophobized CG containing an anti-inflammatory drug was also characterized as a drug delivery device [257].

CG is one of few biopolymers that have been proposed to replace the similar but more popular polysaccharide gum arabic. As a biopolymer with amphiphilic compounds, CG was reported to have about 6% of polysaccharide-protein complex, suggesting that probably the same complex is present in the gum arabic. The similarity of both gums suggests the study of CG in the food and beverage industry as thickening and gelling agent, and as colloidal stabiliser [258].

8. Pectin

Pectin is a complex and heterogeneous polysaccharide located in the middle lamella and primary cell walls of plant tissues, and in fruits and vegetables. The chemical structure of pectin depends on the origin, location in the plant and extraction method, been composed of acidic polymers, known as homogalacturonan, rhamnogalacturonan and xylogalacturonan with several neutral sugars/polymers such as arabinans, galactans and arabinogalactans (attached as side chains). The available data support the highly schematic model of pectin shown in Figure 7. The backbone contains α -(1-4)-linked linear homogalacturonic units alternated with two types of highly branched rhamnogalacturonan regions. The first region is substituted with side chains of arabinose and galactose units, while the second has a highly conserved structure, consisting of the main chain branched with eleven different monosaccharides, including some rare sugars such as 2-O-methylxylose, 2-O-methylfucose, apiose, aceric acid, 2-keto-3-deoxy-d-manno-octulosonic acid, and 3-deoxy-d-lyxo-2-heptulosaric acid. Xylogalacturonan is similar to homogalacturonan except that it is substituted with single β -(1-3)-xylose units or such units substituted with a few additional β -(1-4)-xylose. In all natural pectins, some of the carboxyl groups exist in the methyl ester form [35,47,259].

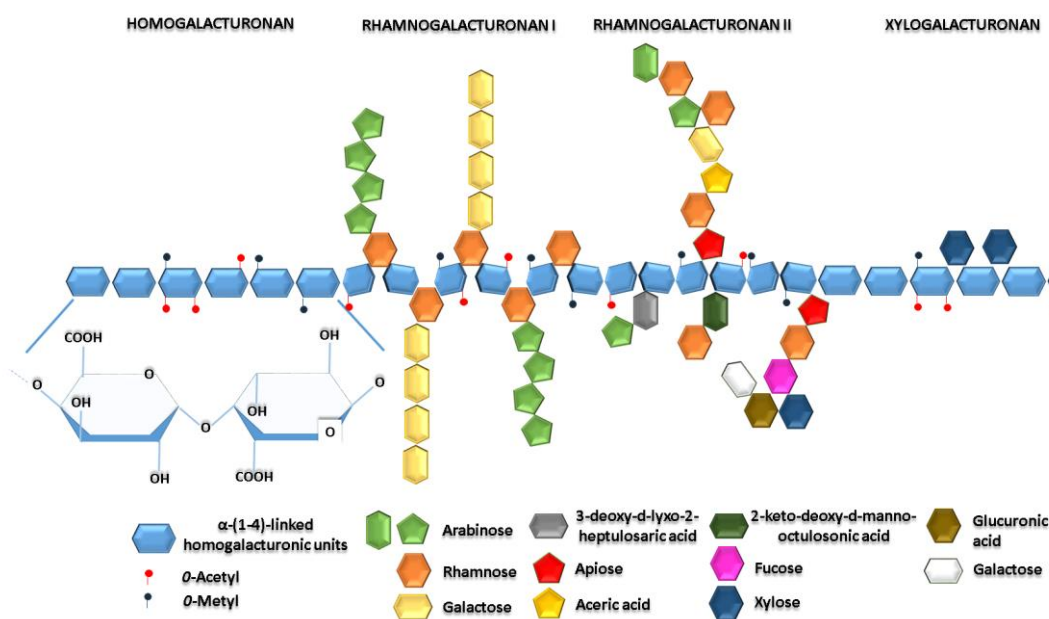


Figure 7. Schematic structure of pectin. The relative abundance of the different types of pectin varies, but homogalacturonan and rhamnogalacturonan I are considered the major components, while xylogalacturonan and rhamnogalacturonan II are minor components.

Pectin has a high molecular weight and can be converted into hydrogels, intended as flexible network of polymer chains that can swell but do not dissolve in water. Pectin solutions at high concentrations and low pH facilitate the formation of coil entanglements, resulting in formation of physical gels. Moreover, water-insoluble gels may be obtained with the use of divalent or trivalent cations. This simple gelling mechanism has raised interest for the preparation of hydrogels for biomedical applications, including drug delivery, gene delivery, tissue engineering and wound healing. It is also important to highlight that the monosaccharide content and the spatial disposition of

the crosslinking blocks in the pectin structure need to be carefully considered when designing pectin gels for specific biomedical applications [260].

Pectins exist with different degrees of esterification. They can be classified as high methoxyl pectin or low methoxyl pectin according to its degree, that yield some differences in their properties, for example, pectins with a high degree of esterification form thermoreversible gels in acidic conditions [47,261].

Pectins are widely used as technological adjuvants in the food industry, fully exploiting their structural diversity. Different structures lead to distinct gelling properties, emulsion and thickening activities, emulsion stabilities, and release effects in complex food matrices. In the pharmaceutical industry, pectin is commonly used as an excipient due to its non-toxicity, low production costs, and gelling activity properties [262].

Edible coatings based on pectin [263,264] and associated with other polysaccharides, including alginate [265] and chitosan [129], were developed in terms of evaluate the coating storage ability on foods and fruits. Pectin containing agricultural by-products are also used as potential sources of a new class of prebiotics known as pectic oligosaccharides [259,266,267]. The impact of protein content and combination mode between protein and pectin on emulsifying properties is one of the most properties studied by the scientific literature [268-270].

The increasing use of pectin in drug delivery is facilitated by the physicochemical properties of pectin. Muco-adhesiveness, ease of dissolution in basic environments, resistance to degradation by proteases and amylases of the upper gastrointestinal tract and the ability to form gels in acid environments, which allows this natural polysaccharide to target different drug delivery formulations. For example, films [271], beads [272], pellets and structures in micro and nanoscale [273-275], into completely different environments such as nasal, vaginal, ocular, gastric and, specially, large intestine [261,276]. The use of pectin-derived drug carries in colon cancer treatments has been extensively considered; pectin is intact in the upper gastrointestinal tract and degraded by specific colonic bacteria [277,278]. Modification of pectin via grafting with poly(N-vinylpyrrolidone) (PVP) has also been reported to form an effective hydrogel that can make effective colon-targeted drug delivery [279]. In terms of the gel-forming capacity, pectin lowers cholesterol by binding the cholesterol and bile acids in the gut, thus promoting their excretion [280-282].

In addition to food and pharmaceutical applications, recent studies reported that pectins showed immunomodulating activities [283-285]. The hydrogel of pectin has been explored in tissue engineering applications for bone cell culture and promoting the nucleation of minerals, and in wound healing applications for binding active drugs or growth factors and protecting against bacteria [260]. Still in view of the wound care, oxidized pectin and carboxymethyl chitosan membranes were developed by in situ cross-linking and demonstrated to be non-hemolytic and cytocompatible [286]. Pectin is a natural anti-glycation agent and has been used beneficially to treat healing damages. Wound dressings of oxidized pectin, gelatin and nonwoven cotton fabric were used as immobilizing supports for nanosilver and ciprofloxacin [287] and aloe vera and curcumin [288] with the important propose to test their viability as effective materials for wound management.

9. Starch

Starch is a biopolymer synthesized in a granular form by green plants for energy storage over long periods. Starch granules consist of two major components, branched amylopectin and linear amylose;

in both cases, the basic structure is composed of α -D-glucopyranose residues, forming α -1,4-glycosidic bonds in linear structure of amylose and additional α -1,6-glycosidic branches in amylopectin molecules. Minor constituents such as lipids, proteins, and minerals are present in starch and the levels vary with the origin. The differences in structure of amylose and amylopectin have indeed significant variance in their properties. Amylose is much more prone to crystallization process, called retrogradation, and can produce tough gels and strong films, while amylopectin could be dispersed in water and retrogrades much slower, which results in soft gels and weak films [35,289].

The predominant model for starch structure is presented in multi-scale, consisting of granules, into which is found growth rings composed of amorphous and crystalline lamellae containing amylopectin and amylose chains [290], as can be observed in Figure 8.

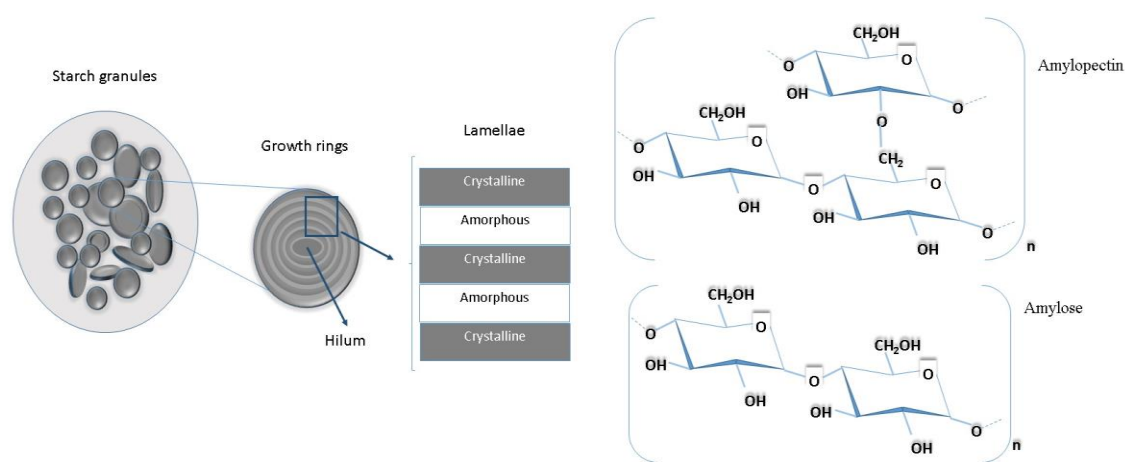


Figure 8. Multi-scale model for starch structure, containing granules, growth rings, amorphous and crystalline lamellae, hilum, and amylopectin and amylose molecular structures.

Starch is an excellent material for biotechnological applications due to its non-toxic, renewable and biodegradable characteristics; however, its direct applications are limited by its poor processability and intrinsic properties, such as thermal, mechanical, and biological properties. Thus, various chemical, physical, and enzymatic modifications or blending with other materials has supplied solutions to achieve properties that are more desirable. Similar to the cellulose (section 4), conventional chemical modifications of starch are performed based on the primary and secondary hydroxyl groups, including esterification, etherification, oxidation, and graft copolymerization [35].

Starch esters are generally prepared by reacting with fatty acids and fatty acid methyl ester in organic solvents [291,292]. Starch esters have been developed for pharmaceutical applications, e.g. used as superdisintegrant and matrix former in capsules and tablet formulations; and for medical application to maintain human colonic function and preventing colonic disease [35,293].

Quaternary ammonium cationic starches, the major commercial starch ethers, are commonly prepared by the reaction of an aqueous alkaline solution of 2,3-epoxypropyltrimethyl ammonium chloride or 3-chloro-2-hydroxypropyltrimethyl ammonium chloride. The quaternary ammonium-substituted cationic starches may form nanoparticles with anionic sodium tripolyphosphate. The nanoparticles could

entrap hydrophobic molecules, providing a great potential as nanosized carrier in health care and environmental sciences [35,294]. Hydroxyethyl starch is semisynthetic starch ether by reacting with ethylene oxide in alkaline medium, and it has been used as a plasma volume expander and cryoprotectant in medicine. A nanocarrier based on hydroxyethyl starch for active receptor-mediated targeting was synthesized [35,295]. The hydroxyethyl starch folic acid conjugate nanocarriers could be of high interest for the development of receptor mediated targeting using polymeric nanocapsules to deliver and accumulate their encapsulated molecules to the targeted area.

Selective oxidation of starch with N_2O_4 or a TEMPO/NaClO/NaBr system can exclusively yield carboxylates on the primary hydroxyl groups. Such oxidation approaches can also be applied to selectively oxidize starch derivatives, which bear another oxidation candidate primary hydroxyl group (e.g. hydroxyethyl starch) [35]. Recently, NaClO oxidation was applied in the aqueous re-dispersibility of starch nanocrystal powder and increased the oxidation degree from 0.41 to 0.581% (w/w), while the applied active chlorine increased from 1 to 4% (w/w) [296].

It is important to note that starches are chemically and/or physically modified to accentuate their positive characteristics, diminish their undesirable qualities (such as high viscosity, susceptibility to retrogradation, and lack of process tolerance), or improve new attributes (retention, film formation, digestibility, solubility, etc.). Acid hydrolysis has been used for a long time to modify starch and its properties because of its simplicity and controllability; recently, the main researches about acid hydrolysis has been applied for preparing starch nanocrystals (SNC). The preparation methods and applications of SNC have been extensively reported by the scientific literature [290,297-300]. In addition to SNC, starch crystallites, microcrystalline starch and hydrolysed starches all refer to the crystalline part of starch obtained by hydrolysis. They differ from each other in the extent of hydrolysis they have undergone (from the most to the least), and have to be distinguished from starch nanoparticles, of which they are just one kind, and which can be amorphous [290].

Because starch is environmentally friendly, nano-scale starch derivatives are suggested as one of the promising biomaterials for novel utilization in foods, cosmetics, medicines as well as various composites. For example, a comparative study was developed with waxy maize starch nano-derivatives extracted through acid hydrolysis and ultrasound treatment, respectively for nanocrystals and nanoparticles. Their application in nanocomposite films was suggested to improve their morphological, structural and thermal behaviour [301]. SNC and nanoparticles were also compared in a rheological characterization of suspensions containing its nano-derivatives under different ionic strength conditions [302]. SNC were also found to serve as an effective reinforcing agent for natural rubber [303], edible films from potato starch [304], and amaranth protein films [305].

10. Conclusions

The aim of this review was to approach the most recent scientific literature dealing with natural polymers, their chemical structure, physicochemical and functional properties, in addition to their biotechnological applications. From the fundamental point of view, it was remarkable to note the preference of industry applications for natural gums when comparable with synthetic materials due to their non-toxicity, low cost, availability, biodegradability and biosafety. The use of nano-tools to process natural polymers, their derivatives or blends, is gaining prominence in the industrial field due to the advantages in the use of nanomaterials sourced from natural origin, since the use of these materials are likely to cause less environmental impact.

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Conflict of interest

Authors have declared that no competing interests exist.

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