Exopolysaccharides in Food Processing Industrials

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Abstract Microbial exopolysaccharides are a class of extracellular carbohydrates based on biopolymeric materials produced and secreted by bacteria, yeast, molds, and microalgae. Cellulose, pullulan, xanthan gum, dextran, kefiran, curdlan, emulsan, alginate, gellan, carrageenans, hyaluronic acid, levan, colanic acid, welan, glucuronides, succinoglycans, and mutan are the exopolysaccharides (EPSs) of different microbial origin. Most of the available EPSs are non-toxic, biocompatible, biodegradable, and obtain from renewable resources. Microbial EPSs display unique functional properties due to their nature and structural composition. The demand for natural microbial EPSs utilization in the food industry due to their unique properties, including emulsifier, gelling agent, and stabilizers. Microbial EPSs and their derivatives have found a wide range of applications in food systems, including fermented dairy products, bakery products, cereal-based products, beverages, delivery of active agents, coatings, and films. This chapter will present a comprehensive overview of the recent developments of EPSs and their potential utilization in the food industry.

Keywords Exopolysaccharides · Hydrocolloids · Functional food · Food ingredients · Delivery systems

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A. K. Nadda et al. (eds.), *Microbial Exopolysaccharides as Novel and Significant Biomaterials*, Springer Series on Polymer and Composite Materials,
https://doi.org/10.1007/978-3-030-75289-7_8

1 Introduction

Microbial exopolysaccharides (EPSs) attract extensive attention in the food industry due to the growing interest in renewable sources. EPSs are considered potentially sustainable alternatives to chemical polymers because they are considered cost-effective, eco-friendly, non-toxic, high efficient, and biodegradable [119]. EPSs are naturally occurring extracellular polymers that are synthesized during the metabolic process of microorganisms, including bacteria, yeast, molds, and algae [12, 43, 45]. EPSs based on their compositions are divided into two groups; (1) homopolysaccharides and (2) heteropolysaccharides. The homopolysaccharides are created by a single type of monosaccharide including, D-glucose or L-fructose. The heteropolysaccharides are composed of several types of monosaccharides, including D-glucose, L-fructose, D-galactose, D-glucuronic acid, L- glucuronic acid, D-mannuronic acid [43, 119]. Cellulose, dextran, curdlan, and levan are examples of homopolysaccharides, while gellan, xanthan gum, and hyaluronic acid are examples of heteropolysaccharides [55]. The EPS production yield and structure depend on culture type, inoculum volume, including carbon and nitrogen source, substrate composition, airflow rate, temperature and pH of cultivating medium, agitation or mixing speed of incubation condition [41, 119]. Microbial EPSs are promising hydrocolloids, used as food ingredients such as stabilizing, gelling, thickening, and binding agents. For instance, pullulan enhanced the pasting and rheological properties of rice starch [23], xanthan gum improved the egg white foaming properties [34], xanthan gum addition into potato starch improved the physicochemical characteristics of gels [42], inulin and xanthan gum in the formulation of custard desserts increased the viscoelastic characteristic of product [131], xanthan gum in developing of low-fat food preparations [48], xanthan gum as gluten replacement [114], xanthan gum for development of low glycemic index food formulations [139], dextran and levan as bacterial EPSs in kefir beverage formulation [51], curdlan in set yogurt formulation [189], curdlan as fat mimetics ingredient for meat products [56], and alginate in low-fat mayonnaise fabrications [101], meat buffers were formulated by using gellan [166], hyaluronic acid and carrageenans for films or hydrogels preparations [30, 192], levan for nanoengineered structures [40] and welan in emulsion stabilization systems [111].

Prebiotics are the indigestible food ingredients that enhanced beneficial microorganisms activity and growth in the gastrointestinal tract [86]. Microbial EPSs are the most promising polysaccharides with prebiotic properties, and pullulan enhanced *Lactobacillus* and *Bifidobacterium* viability in low-fat yogurt [94] as well as; in another study, the prebiotic activity of pullulan were proved in wheat bread [128]. Antimicrobial agents such as metallic nanoparticles [2], bacteriocins [158], plant extracts [89], and essential oils [29] can be added or encapsulated into microbial EPSs for designing food-grade polymers to create an active food packaging system for maintaining food safety and quality during food storage. In contrast to synthetic polymers, biopolymers have the advantage of sustainability and environmentally friendly features. Recently, researchers have focused on biodegradable polymers [8]. Microbial exopolysaccharides are good candidates for the fabrication of high-performance non-toxic polymernanocomposites as well [5]. EPSs in polymer matrix resulted in significant improvement of mechanical, thermal, and barrier properties such as polyvinylalcohol (PVA)-bacterial cellulose nanocrystals (BCNC) [60], hydroxypropyl methylcellulose (HPMC)-BCNC [59], Konjac glucomannan-pullulan [181], pullulan-lysozyme nanofibers [153], packaging paper coated with curdlan and chitosan [17] and nanocomposite of cellulose nanocrystals and kefiran [149] are some examples of engineered nanocomposites with microbial EPSs.

Microbial EPSs also have the potential to produce biofilms and other bioengineered micro-nano structures for use in food applications [4] such as bacterial cellulose olive oil Pickering emulsions [180], pullulan based cinnamon essential oil nanoemulsions [29], astaxanthin encapsulated whey protein isolate-xanthan gum emulsions [15] and probiotics in dextran nanoparticles [86]. Microbial EPSs produced from bacteria as bacterial EPSs including bacterial cellulose [108], and xanthan gum [41], and from yeast-like fungus as fungal exopolysaccharide such as pullulan [155] by fermentation of a wide variety of substrates including organic and inorganic nutrients. The growth media substrates are expensive and increased the cost of microbial EPSs production on industrial scale. Alternative low-cost process substrates have been used for industrial-scale production. Agro-based wastes are composed of food constituents, which can be economically feasible raw materials in growth media with or without additional nutrients [72]. Agri-industrial residues including soya bean oil cake, mustard seed oil cake, rice bran oil cake, and corn steep liquor were used for pullulan production as growth media substrates [150], citrus peels including mandarin, orange, grapefruit, and lemon used for bacterial cellulose [72], waste bread hydrolysate consumed for xanthan gum production [41]. By the way, using industrial wastes utilization in this way could contribute to the waste management systems. This chapter provides an overview of the unique properties and the potential food applications of widely used microbial EPSs in the food industry. The food applications of microbial EPSs are also presented in Table 1.

2 Cellulose

Bacterial cellulose (BC) (β-1,4 linked, D-glucose) is a natural, edible, non-toxic, biodegradable, and biocompatible microbial exopolysaccharide [152]. BC can be produced from different kinds of microorganisms, including *Gluconacetobacter* [142], recently named as *Komagataeibacter, Aerobacter, Azotobacter, Achromobacter, Rhizobium, Alcaligenes, Escherichia, Salmonella, Pseudomonas* [123], *Sarcinia*, and *Agrobacterium* [32]. *Komagataeibacter xylinus* has been used as a model organism for industrial bacterial cellulose production [123]. The choice of bacterial strain is a significant parameter to produce a high yield of bacterial cellulose. The other factor was the growth media; Hestrin-Schramm (HS) medium [70] which was the most used medium for the BC production and alternative carbon (sugar, molasses) and nitrogen (peptone, yeast extract, corn steep liquor, peanut sprout extract) sources were used for the production [32, 162]. The high cost of growth media limited the BC production on an industrial scale. BC can be produced from industry by-products wastes for reducing the cost, such as whey protein from dairy industry [142], wastewater of candied jujube processing industry [105], and Colombian agro-industry waste pineapple peel and sugar cane juice [33]. BC has the same molecular formula $(C_6H_{10}O_5)_n$ of plant cellulose, while BC is pure material without lignin, hemicellulose, and pectin, making the purification easy for application [8]. BC can be used as a multifunctional food ingredient to improve the rheology of food, as a thickening, stabilizing, gelling, suspending agent, as well as in the formulation of low calorie and low cholesterol food product formulations, and immobilization of enzymes, as a nano carrier for encapsulation of food additives and food packaging material [152, 167]. BC is considered as "generally recognized as safe" (GRAS) by the Food and Drug Administration (FDA) in 1992 [167]. The nata de coco was accidentally discovered by Pagsanjan, Laguna in Luzon, Philippines. The first use of BC in food to manufacturing Philippine's traditional sweet candy dessert is called "*nata de coco*". It is prepared from coconut water through a fermentation process by *Acetobacter xylinum*. *Nata de coco is* also produced and consumed in Indonesia as a healthy diet and in East Asian countries [73]. The Philippines was the primary producer of nata de coco with an international market volume of about 6350 tons, with $6.63 billion worth in 2011. The nata de coco exported to the international markets, the major importing countries are Japan, the United States, Canada, Malaysia, and other 40 countries, including the European and Middle East countries [135]. Also, nata de coco industry had export value chains in Vietnam, Thailand, and Indonesia [134]. BC (nata) has been used as a fat replacement in different foods. Lin and Lin [109] were investigated the potential use of BC (nata) as a functional ingredient with Chinese-style meatball. Meatballs were produced with 10, 20, and 30% nata and 20% fat as control. Meatballs containing 10% nata had the same sensory and texture acceptability as control meatballs. A study was carried out by Halib et al. [66], evaluated nata de coco dessert as a possible source of pure bacterial cellulose for research study. In this study, the extracted BC characterized by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The purified BC powder possessed similar FTIR spectra and degradation DTG peak that reported for BC. The food-grade material, nata de coco from local food industries, could be used as a source of BC.

Bacterial cellulose is a natural microbial extracellular polysaccharide. It has unique properties including low density, large surface area, high aspect ratio, high crystallinity, high purity, high water holding capacity, high tensile strength and nanoscale dimension, unique morphology, and 3D nanofibrillar cellulosic network [156, 184], these properties enable BC in a wide range of specific applications in food packaging and food-grade emulsion formulations specifically Pickering emulsions. Pickering emulsions are formed from solid colloidal particles, irreversibly attached at the between oil-water interface [80], depending on the solid particles wettability properties. Pickering emulsions can be either oil-in-water (o/w) or water-in-oil (w/o) emulsions [26]. Several investigations have reported the use of bacterial cellulose nanofiber (BCNF) and bacterial cellulose nanocrystals (BCNC) for stabilization of Pickering emulsions [79, 80, 180] and also Pickering emulsions of BC with other polymers such as BCNC-gelatin for cinnamon essential oil [140]. Bacterial cellulose nanocrystals can be produced from BC nanofibers under controlled acid hydrolysis conditions by chemical treatments [3] and by enzymatic treatments as green nanomaterials [60, 144]. Acid hydrolysis favors the removal of amorphous regions, provides crystal regions, and changes nanocrystals charge density [3]. Hydrochloric acid treatment results in weak surface charge, sulfuric acid-treated samples result in negatively charged sulfate esters on the crystal surface; this charge density affects formation of stable colloidal suspensions and the wettability of nanocrystals at oil-water interface [80].

The BCNCs amphiphilic character, hydrophilicity and hydrophobicity balance, nanocrystals wettability at the oil-water interface, emulsifying properties, crystals morphology, crystallinity, and size variation strongly affect the stability of Pickering emulsions [80, 133]. The emulsifying performance of hydroxypropyl methylcellulose (HPMC), carboxymethyl cellulose (CMC), and bacterial cellulose (BC) for extra virgin olive oil Pickering emulsions formulations were tested via using high shear mixer and ultrasound methods [133]. The BC and extra virgin olive oil Pickering emulsions showed better stability than the other commercial cellulose and were not affected by pH, temperature, and ionic strength changes. However, HPMC and CMC extra virgin olive oil Pickering emulsions were more sensitive to environmental stresses [133].

In another study, the possible use of BC and BCNCs in the stabilization of olive oil Pickering emulsion were evaluated [180]. Regarding this study results, the BCNCs with 259.6 nm particle size, −34.8 mV zeta potential, and 89.6% crystallinity index were hydrolyzed with sulfuric acid, acid treatment followed by the hydrogen peroxide oxidation. The olive oil Pickering emulsion formation with BC and BCNCs was proved by optical and fluorescence microscope. The BC oil Pickering emulsions showed better stability than the BCNCs towards the change of pH and ionic strength. Results proved that BC and BCNCs particles could be adsorbed at the oil and water interface to form the Pickering emulsions. The formed particle-stabilized emulsions showed better colloidal stability against the coalescence [180].

Apart from the BC fibers and crystals outstanding unique properties, BC was non-toxic, edible, available from renewable sources, biocompatible, and biodegradable polymer for encapsulation purposes. The BC engineered structures can be used as delivery systems for the encapsulation of bioactive substances and provide stability against environmental degradation, improving the stability of encapsulated food ingredients for food applications [8]. The BC and BCNCs as carriers for bioactive agents as Pickering emulsion could be used directly into the food matrix to produce functional foods and into the films and coatings solutions for food packaging applications. BC has great potential to use as the support material for films [49], foams, coatings, and rapid and simple sensing devices [92], due to its three-dimensional nanostructure, the high specific surface area, high water holding capacity, high tensile strength, besides bacterial cellulose films has the characteristic of transparency, flexibility, and hydrophilicity. In addition to BCs renewability and sustainability, its appealing characteristics such as high crystallinity and high mechanical strength enable to use BC as reinforcing agents in high-performance nanocomposite materials and eco-friendly materials for various applications, especially food packaging applications [9].

Most microbial contamination and deterioration reactions occur on the food surface [63]. Food packaging materials should exhibit good barrier and mechanical properties for preserving food quality and safety. Biobased polymers have not fulfilled these requirements, such as commercially available plastic packagings. BC and BCNCs are used as nanofiller, nano reinforcements with a wide range of polymers to develop nanocomposites to improve the polymers barrier and mechanical properties for packaging materials [8, 28]. George et al. [60] developed a reinforced Polyvinylalcohol (PVA) matrix with BCNC to generate polymer nanocomposites. BCNC was manufactured from enzyme hydrolysis with desirable properties, 100–300 nm length, and 10–15 nm diameter. BC-PVA nanocomposite display improved thermal stability and mechanical properties [60]. BCNC obtained by hydrochloric acid hydrolyzes is used as reinforcing hydroxypropyl methylcellulose (HPMC) polymer material. BCNC resulted in remarkable improvement in the tensile strength and modulus of HPMC, while the incorporation of 2–4% BCNC reduced the elongation properties [59]. The nanocomposite of bacterial cellulose nanofibrils (BCNs) supported zein nanoparticles (ZN) was developed by Li et al. [102]. The resulting BCN-ZN nanocomposites possessed improved mechanical and thermal properties. The incorporation/encapsulation/embedded antimicrobials into the food packaging polymers can reduce or retard the spoilage or pathogenic microorganism [2].

BC was used in a wide range of applications because of BCs outstanding properties, whereas BC has no antimicrobial property. Gao et al. [57] developed an antimicrobial BC film with nisin via the co-culturing method with nisin producing strain *Lactococcus lactis*. Jebel and Almasi [75] described a novel monolayer and multilayer of BC films with zinc oxide (ZnO) nanoparticles. Bacterial cellulose-containing antimicrobial composite films were also developed with a wide range of organic and inorganic antimicrobial agents such as PVA-BC with potassium sorbate [77] and silver nanoparticles incorporated chitosan-BC [146]. The bacterial cellulose films with antimicrobial properties are obtained with silver nitrate ($AgNO_3$). BC matrix was used for the stabilization of silver nanoparticles (AgNPs). An antimicrobial nanocomposite of bacterial cellulose silver extended tomatoes shelf-life up to 30 days [2]. The efficacy of nisin immobilized bacterial cellulose (BC) films was tested on processed meat [126]. Bacterial cellulose films were obtained by *Gluconacetobacter xylinus* K3 with Corn Steep Liquor-mannitol medium. BC-nisin composite films were prepared to immerse BC films into nisin solution for the absorption of nisin into the films. Nisin incorporated bacterial cellulose films that possessed antimicrobial activity on agar media and significantly reduced the artificially inoculated *L. monocytogenes* population on frankfurters as a food model. In addition, Zhu et al. [191] fabricated BC embedded ε-polylysine (ε-PL) casing for sausage packaging. The composite of BC/ε-PL was obtained soaking of BC into ε-PL solution to allow absorption of ε-PL through cellulose film. The composite film had remarkable antimicrobial activity against *E. coli* and *S. aureus* on agar media and sausages. The population of bacteria on sausage samples treated by BC/ε-PL was significantly lower than the BC films during 18 days storage at 4 °C. Bandyopadhyay et al. [11] fabricated films from BC and guar gum (GG) based polyvinyl pyrrolidone-carboxymethyl cellulose (PVP-CMC). The films were tested for shelf-life analysis of berries. Berries were packed with PVP-CMC, PVP-CMC-BC, PVP-CMC-GG, and PVP-CMC-BC-GG films. The weight loss of berries packed with PVP-CMC-BC-GG films was lower than the other films due to the least water vapor permeability (WVP) and oxygen permeability (OP) values. Yordshahi et al. [183] developed antimicrobial BC film as a carrier for postbiotics lactic acid bacteria. The antimicrobial effect of nanopaper with BC and postbiotics lactic acid bacteria tested on ground meat, lactic acid bacteria immobilized BC films decreased the *L. monocytogenes* growth on ground meat and total mesophilic and psychrophilic count during 9 days of storage at 4 °C. Because of BC outstanding properties with the high specific area and high porosity, BC would be used for intelligent food packaging applications as intelligent labels or sensors for freshness monitoring. In the study of Kuswandi et al. [92], edible pH sensor developed by BC membrane immobilized red cabbage anthocyanins for intelligent food packaging systems. The developed system can distinguish fresh milk from spoilage. Moreover, Mohammadalinejhad et al. [115] proved that *Echium amoenum* anthocyanins immobilized BC films may be used for development of novel non-destructive intelligent food packaging systems for monitoring the freshness or spoilage of shrimp as colorometric pH indicator. There are a wide range of promising applications for utilization of BC in food industry due to its purity, biocompatibility, high water holding capacity, mechanical strength, food-grade material, network structure, and better emulsifying capacity; however, production yield, quality, and the demand properties of end product, price of growth medium are the challenges of BC to be overcome for food applications.

3 Pullulan

Pullulan is a non-toxic, biodegradable, biocompatible water-soluble neutral edible, extracellular exopolysaccharide commercially produced by a yeast-like fungus *Aureobasidium pullulans* [21, 67]. Pullulan has a linear glucan structure consisting of maltotriose repeating units [155]. Pullulan can be produced from other microbial sources, including *Cytaria harioti, Cytaria darwinii, Cryphonectria parasitica, Teloschistes flavicans, Rhodosporidium paludigenum,* and *Rhodotorula bacarum* [154]. Pullulan has a potential application for food applications such as a thickener, stabilizer, binder, dietary fiber, texture improver, prebiotic, low-calorie food ingredient [94, 155]. Pullulan dietary fiber effects have been tested on fried potato starch [24] and rice starch digestibility [22]. Pullulan, a natural, odorless, tasteless polymer, is used for food packaging applications in developing edible film and coating formulations. Pullulan films and coatings with antimicrobial agents have great potential to reduce microbial spoilage and extend food products shelf-life. Chu et al. [29] prepared antimicrobial pullulan coatings with cinnamon essential oil nanoemulsion. Pullulan-cinnamon essential oil nanoemulsions coatings significantly decreased the total aerobic counts and yeast and mold counts of strawberries during room storage. Kraśniewska et al. [89] manufactured a pullulan coating enriched with leather bergenia leaves extract. Pullulan-leather bergenia leaves extract films antimicrobial efficacy was tested on artificially inoculated peppers with *Aspergillus niger* and *Staphylococcus aureus* and apples with *Aspergillus niger*. Pullulan-leather bergenia leaves extract coatings showed a high inhibitory effect on fungal contamination of apples, fungal, and peppers bacterial contamination. In another shelf-life study, carried out by Kumar et al. [91], chitosan-pullulan composite edible coatings supplemented with pomegranate peel was developed to enhance the quality and shelf-life of green bell paper at room (23 ± 3 °C, RH: 40–45%) and cold temperatures (4 ± 3 °C, RH: 90–95%) for 18 days of storage and no adverse effects were observed on sensory attributes during storage. Wu et al. [177] used *Laminaria japonica*-derived oligosaccharides in pullulan coating for cherry tomatoes preservation. The study performed by Yan et al. [181] improved strawberries' qualities during the storage period with Konjac glucomannan and pullulan composite films.

The efficacy of nisin embedded amaranth protein isolate-pullulan electrospun nanofibers was assessed on apple juice and fresh cheese as a real food model [158]. Fresh cheese and apple juice artificially inoculated with *Salmonella Typhimurium, L. monoctogenes*, and *L. mesenteroides*. Amaranth protein isolate-pullulan nanofibers showed satisfactory antibacterial effects against all bacteria. This study confirmed that nisin encapsulated amaranth protein isolate-pullulan nanofibers potential in controlling the post contamination.

Pullulan potential prebiotic properties were investigated in low-fat yogurt. The viability of *Streptococcus thermophilus*, *Lactobacillus*, and *Bifidobacterium* in the presence of pullulan at 0.5–2% in low-fat yogurt and pH changes during storage at 4 °C for 28 days were investigated [94]. Pullulan addition to reduced-fat yogurt enhanced the viability of *Lactobacillus* and *Bifidobacterium*, however, had no effect on the viability of *Streptococcus thermophilus*. Pullulan addition improved the texture properties but had an adverse impact on sensory attributes in low-fat yogurt. This study demonstrated the pullulan protective effect on the viability of probiotic bacteria for health-promoting properties.

4 Xanthan Gum

Xanthan gum is a charged heteropolysaccharide polymer, which is produced by the *Xanthomonas campestris*. The other Xanthomonas strain types such as *X. axonopodis pv. vesicatoria*, *X. Hortorum pv. pelargonii*, *X. Axonopodis pv. begoniae* and

X. campestris have been used for xanthan gum production [41]. Global production of xanthan gum exceeds 50000 tons/year with 600 and 800 million dollars/year market value [161].

Xanthan gum is an important microbial exopolysaccharide and widely used in the food industry due to its unique properties, including thickening properties [27], film-forming properties [90], and other applications, including a stabilizing agent for emulsions [170], nano-micro carriers for active agents [122] and as functionality enhancers [139]. Xanthan gum addition to the pasteurized egg white foam with Persian gum enhanced the foam texture and stability [34].

Edible coatings can be applied in different methods including, dipping, spraying, and coacervation. The study of Lara et al. [97] investigated the effect of xanthan gum-based edible coatings in the spraying method to improve the storage stability of fresh-cut lotus root. Xanthan gum, citric acid, and glycerol contained spraying solutions that prevent microbial growth, decreased the enzymatic browning, and enhanced the shelf-life of fresh-cut lotus root post-harvest storage. Cho and Yoo [27] determined the impact of commercially available food thickeners, including xanthan gum, guar gum, dextrin, and carboxymethyl cellulose, in cold beverage preparations. The thickened beverages prepared with xanthan gum possessed desired rheological properties and improved the swallowing ability. The study of Espert et al. [48] evaluated the palm oil in vitro digestion in the presence of xanthan gum. The impact of xanthan gum was significant in vitro digestion system, and the xanthan gum matrix remarkably reduced fat digestion.

The texture of the cake, pasta, and bread is considered a critical quality characteristic of these products; hydrocolloids such as xanthan gum are widely used to formulate bakery products. Milde et al. [114] developed a gluten-free pasta with cassava starch, cornflour, and xanthan gum. In the pasta formulation, the presence of 0.6% xanthan gum enhanced pasta dough handling, decreased cooking loss, and improved physical and textural properties. Mohammadi et al. [116] optimized gluten-free flatbread formulations, which included rice flour, corn starch, soy flour, xanthan gum, and also xanthan gum-carboxymethyl cellulose. The highest dough yield, bread yield, and lowest bread weight loss obtained with xanthan gum and xanthan gum-carboxymethyl cellulose combination bread formulations. In another study, the presence of 1% xanthan gum in sponge cake formulation with wheat flour and corn starch improved the hardness of the product but decreased the overall acceptance scores for sensory evaluation [130]. The other food applications of xanthan gum are; Zhao et al. [190] showed the potential of xanthan gum as sodium salt substitute in the low sodium meat products formulations, Santos et al. [147] developed food grade Pickering emulsions formulations with zein-xanthan gum, and sunflower oil, Sharma and Rao [151] developed the xanthan gum embedded cinnamic acid edible coatings for prevented browning and prolonged the shelf-life of fresh-cut pears.

5 Dextran

Dextran (α-1,6-linked glucan) is a homopolysaccharide composed of D-glucose units [176], produced by *Leuconostoc* spp, *Streptococcus* spp, *Weissella*, *Pediococcus* and *Lactobacillus* genera of lactic acid bacteria [13, 69, 88, 119]. Lactic acid bacteria produced a wide variety of different EPSs, including homopolysaccharides and heteropolysaccharides. Dextran, levan, kefiran, and hyaluronic acid are the LAB belonging EPSs [117]. Dextrans texturizing, emulsifying, prebiotics, cloud forming, edible coating properties are the potential applications of dextrans in the food industry [39, 46, 164]. In the baking industry, hydrocolloids have been used to enhance the dough and bread-making process textural and rheological properties [164] and bakery products shelf-life [176, 187]. Microbial EPSs from lactic acid bacteria during sourdough fermentation has the ability to act as hydrocolloid to improve the rheology, texture, and mouth feel properties of fermented dairy products and bakery products in the food industry [14, 44, 164].

Many studies have been conducted on the application of dextran in the bakery industry [13] to determine the prebiotic function of dextran from *Weissella cibaria* RBA12 isolated from pummelo, and its potential application in sourdough fermentation [145] tested the dextran as an alternative of commercially available hydrocolloids in gluten-free bread. Dextran produced by *Weissella confusa* (*W. confusa*) improved quality. It extended the shelf-life of Chinese steam bread with acceptable sensory attributes [164], and in the study of Wang et al. [174] it was reported that the improvement of wheat-fab a bean composite bread quality was due to dextran synthesized in situ *Weissella confusa*, and also wholegrain sorghum bread formulations improved with *W. confusa* [172]. In addition, dextran could be purified from a wide variety of sources with multifunctional properties in different kinds of food applications. Du et al. [44] obtained dextran from *Leuconostoc pseudomesenteroides* from the homemade vine with antioxidant property.

6 Kefiran

Kefiran is an extracellular polysaccharide from lactic acid bacteria during kefir production [149]. Kefiran is available in kefir grains and Lactobacillus species such as *L. kefir*, *L. parakefir*, *L. kefiranofaciens*, *L. brevis,* and *L. delbrueckii subsp. bulgaricus* [95, 118]. Kefiran has potential applications in producing food products, including edible films [61], a delivery system such as doxycycline antimicrobial agent embedded kefiran nanofibers [35], and green nanocomposites with cellulose nanocrystals and kefiran [149].

7 Curdlan

Curdlan is a water-soluble bacterial linear homopolysaccharide composed of repeating unit of (1 → 3)-β-glucan produced by *Agrobacterium* spp. (formerly *Alcaligenes faecalis var. Myxogenes*) [113, 119, 186], *Rhizobium* spp., *Cellulomonas* spp. are the other curdlan producing microorganisms [58].

Curdlan is widely used in the food industry as a stabilizer, thickener, and texturizer and approved by FDA (Food and Drug Administration) as a food additive [186]. Due to its unique properties, including high water holding capacity, rheological, gel-forming, textural improving properties, and freeze-thawed properties, curdlan has been used as a critical ingredient in the food industry to improve the quality of the various type of food products [25]. Textural and cooking qualities are the key quality for the noodles. Gao et al. [58] evaluated the noodle quality that was prepared with curdlan. Regarding the results, the use of curdlan in noodles formulations significantly improved the eating quality and textural properties. In another study, the addition of curdlan into potato starch noodles enhanced the textural properties and increased the syneresis [173]. Liang et al. [106] described how curdlan addition could minimize the effect of curdlan on the quality of frozen cooked noodles during frozen storage. The other important food applications are, curdlan and chitosan coatings improved the mechanical and barrier properties of packaging paper [17], curdlan has been used as a fortifier in a set of yogurt [189], the study of the Funami et al. [56] assessed the possibility of curdlan as fat mimetics ingredient for sausages.

8 Emulsan

Emulsan is an extracellular polysaccharide composed of sugar backbone with fatty acids produced by *Acinetobacter* spp., including *A. venetianus*, *A. calcoaceticus* [20, 78]. Emulsan has potential applications as biosurfactants [129] in the food industry.

9 Alginate

As a popular exopolysaccharide, alginate structure includes two main compounds: *β-D*-mannuronic acid units and α-*L*-guluronic acid units. These acid units are linked by α-1,4 glycosidic bonds. Alginate is collected from various kinds of brown seaweeds and species of *Pseudomonas* and *Azetobacter* also synthesize alginate as an exopolysaccharide [68]. *Pseudomonas* species that are able to produce alginate are known as *P. aeruginosa*, *P. fluorescens* and *P. syringae* [16].

Bacteria cells can adhere to solid surfaces and adhesion process occurs easily in the presence of some EPSs such as alginate. For instance, the attachment of *P. aeruginosa* to solid surfaces was improved by alginate synthesized in the medium. Biofilms created by exopolysaccharide can contribute to overcoming electrostatic repulsion between the bacteria cells and the surface. Hence, alginate has a significant function in the development of biofilms by species of *P. aeruginosa* [16]. Alginates are purified from these medium created by various bacteria species and the production of alginate is commercially performed by using different species of brown algae such as *Laminaria digitata*, *Laminaria japonica, Ascophyllum nodosum*, and *Macrocystis pyrifera*. Extracts obtained from these species were treated with alkali solutions such as NaOH. At the end of purification steps, sodium alginate is obtained in powder form [99].

Alginates are able to produce gels when the medium including divalent cations such as calcium ions. Interaction between alginate and divalent cations is called crosslinking and that is prefered between G blocks and divalent cations. Therefore, guluronate content of alginate is proportional to the gel strength [52]. Alginate has considerable properties as gelling agent, thickening, stabilizing, emulsifying agents, and encapsulation. Besides that, it is a biocompatible and biodegradable material used as a biopolymer, especially for food coating exopolysaccharide [141].

Alginates are commonly used in many industrial processes. In food industry, alginates have been utilized as thickener, emulsifier, and stabilizing agents. The applications of alginate in food products are related to its physical properties. These physical properties come from its unique chemical structure. The α-*L*-guluronic acid units known as G blocks and *β*-*D*-mannuronic acid units known as M blocks defined the functional properties of alginate. In terms of gelling property, G blocks play an important role by binding Ca^{2+} or H^+ binding that results in gel formation. In the food industry, alginate is well known as thickening agent because of its ability to form gels, which are heat stable, at low temperature in the absence of heating or at low pH medium or in the presence of calcium [141]. Ca-dependent gelation and gel properties of alginate are significantly influenced by intrinsic factors including molecular weight, guluronic acid percentage, the length and distribution of Ca-binding blocks, and extrinsic factors such as concentration of alginate, concentration of calcium ions, ion strength, pH, and temperature. Alginate having high molecular weight offers more calcium-binding sites that develop rheological properties of the gels and improve viscosities. Increase in guluronic acid percentage increased the stability and mechanical strength in terms of Ca-dependent gels [19].

Considering the role of alginate in the viscosity properties of foods, diverse food formulations like ice cream, jam, jellies, mayonnaise, salad dressing, desserts, cakes, and candies have been produced. In low-fat mayonnaise formulations, fat reduction affected the textural properties of product and the application of alginate-based gel systems were investigated as alternatives to produce low-fat mayonnaise. Li et al. [101] performed the production of low-fat mayonnaise by emulsifying the oil molecules in the gel medium created by using alginate and alginate stabilized gel-based emulsion produced by using alginate (2%) and Tween

80 (0.5%). Fat droplets in these kinds of products have an important structural function and thus development of low-fat formulation is a challenging issue. Alginates take part in formulations as an alternative ingredient to reduce the amount of fat in the product while maintaining the textural properties of the product. Main advantage of alginate-based gels over other polysaccharide gels is thixotropy, shear-thinning property, but one disadvantage is the formation of weak hydrogels [182]. In the study, it was mentioned that mechanical strength of alginate-based gels was enhanced by using with different polysaccharides such as cellulose, chitosan, pectin, and others. Thus, alginate was combined with glucomannan in different ratios in order to produce low-fat mayonnaise. It was investigated glucomannan addition to alginate at high concentration as 4% considerably enhanced the strength of alginate-glucomannan matrix that forms a complex gel structure. Moreover, the prepared low-fat emulsion gels including alginate and glucomannan indicated good thermal stability after heating at 100 °C for 30 min and freeze-thaw stability after freezing the gels at −18 °C for 24 h [182]. Alginate is also used to replace milk fat droplets to obtain low-fat dairy products due to the higher water-binding capacity of alginate. Sodium alginate was used in the production of Cheddar cheese having low-fat content and its usage improved textural properties. Four levels of sodium alginate 0.12, 0.17, 0.18, and 0.23% were investigated as an ingredient to replace fat content of Cheddar cheese until 91% fat reduction. During ripening of 180 days, fat reduction by addition of alginate resulted in improved textural properties by increasing hardness and microstructural properties, but poor color development [84]. In recent years, low-fat meat products have become more popular and are preferred by consumers. Alginate is one of the hydrocolloids used in low-fat emulsion meat products in order to replace fat by maintaining the quality [82]. The effect of substitution of pork back-fat with alginate solution at 0, 25, 50, 75, and 100% ratios on the quality characteristics, protein conformation, and sensory attributes of frankfurters were evaluated [82]. When the use of sodium alginate solution was 25 and 50% ratios, the cooking yield, emulsion stability, and color values of frankfurters were not significantly different. Texture properties including hardness, springiness, cohesiveness, and chewiness of frankfurters produced by 50% pork back-fat replacement with sodium alginate solution had significantly higher values than others [82].

As a gelling agent, alginate forms stable gels at a wide range of temperatures and low pH conditions. Alginate is widely used in the production of ice cream products for functions such as thickening, stabilizing, controlling viscosity, shrinkage, and ice crystal formation [137]. Moreover, alginate has also been used to obtain hydrogels maintaining viability of probiotic bacteria in low acid medium that simulates gastric juice. Encapsulation of probiotic bacteria, *Bifidobacterium breve*, was carried out by alginate-based capsules and viability of probiotics was enhanced in various pH environments simulating gastric and intestinal medium [104]. Addition of *Lactobacillus rhamnosus* and *Lactobacillus casei* into ice cream in free and encapsulated form by using alginate and chitosan were investigated. Encapsulated *L. rhamnosus* was preserved at low temperatures, but the *L. casei* indicated greater viability during the encapsulation as well as in the gastrointestinal environment [50].

Alginate is being an attractive polysaccharide used for edible films and coatings of foods because of its film-forming ability with non-toxicity and low price. Among the different kinds of alginate salts, sodium alginate is commonly used for producing water-soluble, tasteless, odorless, glossy, and flexible edible films with low permeability to oxygen [165]. Alginate-based biodegradable coatings present an alternative to substitute synthetic coatings for maintaining the quality of fresh fruit and vegetables after harvesting. One disadvantage is poor moisture barriers of edible films produced from alginate due to its hydrophilic structure. However, addition of calcium ions improves the water-resistance of alginate films [143]. A number of studies in the literature have presented the potential of alginate-based edible coatings for maintaining quality attributes of fruit and vegetables such as grapes [87], peach [103], pineapple [7], plum [168], mushroom [76], and arbutus berry [62]. Alginate based coatings have been commonly used as carriers of active ingredients to increase shelf-life and improve quality properties of foods [165]. Recent investigations in literature focus on nanoemulsion alginate coatings in which active ingredients exhibit better properties. Effectiveness of alginate-based nanoemulsion coatings incorporated with sweet orange essential oil were evaluated in terms of antibacterial and antibiofilm activity against *Salmonella typhi* and *Listeria monocytogenes* as well as coating effect on quality attributes of tomatoes during storage at 22 °C. Alginate nanoemulsion indicated antibacterial property against *S. typhi* and *L. monocytogenes* and increased the shelf-life of tomatoes by delaying spoilage caused by the bacteria. In addition, the coating significantly enhanced firmness and reduced weight loss of tomatoes by delaying ripening [38]. Application of alginate-based nanoemulsion coating incorporating lemongrass essential oil at the concentrations of 0.1 and 1% were investigated on fresh-cut apples stored at 4 °C for 14 days. In terms of the quality parameters including weight loss, pH, and acidity, formulation incorporating 0.1% essential oil content was found to have positive effects compared to high essential oil content (1%) [31]. Cinnamon essential oil nanoemulsions were incorporated into alginate-based biocomposite films [54]. In this study, developed biocomposite films including 20% cinnamon essential oil nanoemulsion indicated antibacterial activities against *Salmonella typhimurium, Bacillus cereus, Escherichia coli, and Staphylococcus aureus.*

10 Gellan

Gellan is a kind of gum formed by bacterium *Sphingomonas elodea* (ATCC31461), also called as *Pseudomonas elodea*, through aerobic fermentation. Gellan is one of the EPSs which has ability to form gel in a wide range of conditions such as low concentrations and acidic medium [110]. Structurally, gellan could be in two different forms which are high acyl (HA) and low acyl (LA) gellan. The structure of HA and LA gellan is mainly a linear tetrasaccharide repeat unit of two glucose, one glucuronate, and one rhamnose units [185]. In the tetrasaccharide repeating sequence of gellan, three of the four glycosidic linkages have equatorial bonds at first and fourth carbon atoms of the participating residues. The rest of linkages in the gellan exhibits a systematic "twist" in direction of the chain which ensures helix structure of gellan. The water-based solution of anionic polysaccharides such as gellan present cations which are counter ions to the charged groups of the polymer chains. The balance of positively-charged ions in the solution is provided by interaction with negatively-charged polymer chains. Linear polyanion charge intensity and the charge of individual cations state the strength of this interaction [120].

Gel formation ability of polysaccharides differs from each other. Some of that, such as carrageenan, gellan, and curdlan, are able to form a gel by means of heating and then cooling. Others, such as alginate, LA gellan, and high methoxyl pectin, form a gel at specific conditions including temperature, types of cations, and pH [185]. Different factors should be considered in terms of gelation mechanisms. Gelation process takes place by aggregation of double helices of gellan. It is explained that pH reduction assists aggregation and gelation by means of decreasing the negative charge on the polymer which results in the decrease in electrostatic repulsion between the helices. Some of the cations can bind the helices in defined sites related to carboxylate groups of polymer, and thus decreasing electrostatic repulsion. Increase in ionic size of cations increases the strength of binding ($Li^+<Na^+<K^+<Rb^+<Cs^+$) [120]. Due to its rheological properties, gellan has been commonly used in food products. Generally, food gels are classified as fluid gels, soft gels, and hard gels. Even though xanthan gum is commonly used in weakly gelled foods, such as salad dressings, gellan is used as a gelling agent to form soft and firm hydrogels in foods such as beverages, desserts, jams, and jellies. Low concentration of gellan is applied to form fluid gels in diverse types of fruit juices and beverages. In order to form soft and firm gels in foods such as desserts and jellies, higher concentration of gellan are required [185].

Regarding the food applications of gellan, studies in the literature have investigated the effect of gellan addition in food formulations from different perspectives. Schelegueda et al. [148] evaluated low-sugar content food model systems developed by using natural additives having different roles. One of the additives was gellan, used as gelling agent, xylitol, used as water activity depressor, and natamycin, used as an antimicrobial agent. Addition of gellan at two different concentrations(0.90 and 1.80 g/100 g) was investigated with the combination of other additives. In the model food system, growth of *Zygosaccharomyces bailii* was inhibited by highest gellan concentration at the beginning of storage. However, consumption of nutrients in the medium leads to the utilization of gellan as an energy source by yeasts. It was also explained that higher level of gellan application with natamycin resulted in weak structure in the gel. Effects of low acyl (LA) and high acyl (HA) gellan on the thermal stability of anthocyanins in model beverage systems was investigated [179]. It was indicated that gellan addition maintained thermal stability of anthocyanins during heat treatment and HA gellan provided significantly higher stability improvement than LA gellan. It is probably due to higher degree of acylation in the HA gellan. Acyl

Table 1 Food applications of microbial EPSs

EPS	Sources	Applications in food industry	References
Cellulose	*Komagataeibacter, Aerobacter, Azotobacter, Achromobacter, Rhizobium, Alcaligenes, Escherichia, Salmonella, Pseudomonas, Sarcinia, Agrobacterium, Dickeya, Rhodobacter*	Gelling agent, emulsifying agents, delivery of bioactive agents, coatings, and films	[32, 92, 107, 123]
Pullulan	*Aureobasidium pullulans, Cytaria harioti, Cytaria darwinii, Cryphonectria parasitica, Teloschistes flavicans, Rhodosporidium paludigenum, and Rhodotorula bacarum*	Delivery of bioactive agents, coatings films, and prebiotic properties	[21, 67, 154]
Xanthan gum	*Xanthomonas axonopodis pv. vesicatoria, Xanthomonashortorum pv. pelargonii, Xanthomonas axonopodis pv. begoniae and Xanthomonas campestris*	Gelling agent, thickening, delivery of bioactive agents, coatings, and films, sodium salt substitute, gluten-free food formulations	[41, 47, 98, 151, 190]
Dextran	*Leuconostoc spp, Streptococcus, Weissella, Pediococcus, and Lactobacillus genera of lactic acid bacteria (LAB)*	Functional food applications, texturizing, emulsifying, prebiotics, cloud forming, edible coating	[13, 39, 46, 88, 164]
Kefiran	*Lactobacillus species such as Lactobacillus kefir, Lactobacillus parakefir, Lactobacillus kefiranofaciens, Lactobacillus brevis, and Lactobacillus delbrueckii subsp. bulgaricus*	Delivery of bioactive agents, coatings, and films	[35, 61, 95, 118]
Curdlan	*Agrobacterium sp*., *Alcaligenes faecalis var. Myxogenes, Rhizobium spp, Cellulomonas spp*	Texturizing, emulsifying, delivery of bioactive agents, coatings, films, and fat mimetics	[56, 58, 113, 173, 186, 188]
Emulsan	*Acinetobacter sp, including A. venetianus, A. calcoaceticus*	Adsorption, biosurfactants	[20, 78, 129]
Alginate	Species of *Pseudomonas* and *Azetobacter*	Gelling agent, thickening, stabilizing, emulsifying agents, encapsulation, biodegradable coating	[68, 141]
Gellan	*Sphingomonas elodea, Pseudomonas elodea*	Gelling agent to form soft and firm hydrogels in foods, edible films for food packaging applications	[110, 185]

(continued)

Table 1 (continued)

EPS	Sources	Applications in food industry	References
Carragenan	Seaweeds of the class Rhodophyceae	Gelling, thickening, emulsifying agent, texture enhancers, and stabilizers in food products	[18]
Hyaluronic acid	*Streptococcus* species such as *Streptococcus equisimilis, Streptococcus pyogenes, and Streptococcus equi*	Hydrating agent in cosmetics and pharmaceuticals, biocompatible films, or hydrogels	[74, 163]
Levan	Lactobacillus johnsonii and Lactobacillus gasserii, Bacillus subtilis, Aerobacter levanicum, S. salivarius	Emulsifier, stabilizer, thickener, encapsulating agent, and carrier for flavors, inhibition hyperglycemia induced by diabetes	[36, 159]
Colanic acid	*E. coli* and also other species of Enterobacteriaceae family	Gelling agent in cosmetics and personal care products	[132, 160]
Welan	*Sphingomonas* sp., *Alcaligenes* sp.	Thickening, binding, and emulsifying agent in food products	[83]

groups in gellan molecules tend to regulation of structure into more extended frame. Thus, LA gellan molecules showed more strict arrangement. In another study, meat buffers were formulated by using gellan in order to reduce fat and sodium content [166]. Texture properties of reduced fat and sodium meat batters were evaluated by usage of gellan in the study. Hardness of samples was highest in the control samples while rigid structure decrease with the reduction in fat content and increased gellan content. Moreover, gellan is newly used gum in edible films developed for the applications of food packaging. For instance, gellan is used as an edible film matrix for carrying of ascorbic acid for improving food quality by antioxidant activity. Ascorbic acid degradation in the developed gellan based edible film indicated a pseudo-first order kinetics and it was indicated that ascorbic acid 100%-retained in film matrix after film casting [100]. Production and storage of gellan based edible films with the gellan concentrations of 0,0.02, 0.04, 0.06, 0.08, and 0.10% were investigated by Xiao et al. [178] and it was found that concentration of 0.08% gellan in edible films presented a desirable tensile strength and perfect film barrier properties. Storage of gellan based films was also investigated under four different conditions including refrigerated conditions at 0 °C, supermarket storage environment at 6 °C, room temperature at 25 °C, and high temperature at 35 °C [178]. Under storage conditions of room temperature and high temperature, higher water vapor permeability was observed due to the increase in velocity of gellan and other molecules. In another study, LA and HA gellan based edible coatings were optimized for application on ready-to-eat mango bars. As an independent variable, gellan concentration considerably affected the coating thickness. Gellan coating of mango bars improved sensory characteristics, color, and volatiles of fruits during storage [37].

Oil-in-water emulsions including 30% sunflower oil were stabilized by using HA gellan at different concentrations changing from 0.01 to 0.2%. HA gellan was effective to stabilize emulsions at concentration above 0.05% and it was compared with LA gellan at the same conditions. LA gellan was not found to be effective in stabilization of emulsions. It was suggested that HA gellan can be used as a potential ingredient to stabilize food emulsions [171]. Gellan was used with microcrystalline cellulose in order to develop physical and thermal stability of ginkgo beverages. The stability of ginkgo beverage was evaluated by characteristics of particle size, size distribution, zeta potential, and rheological properties. The study indicated that gellan with a small amount of 0.05 or 0.08% contibuted effectively to beverage stability compared to the larger amount of gellan by decreasing particle size and increasing zeta potential [127]. In yogurt and yogurt-based beverages, serum separation is one of the quality defects delayed by using hydrocolloid stabilizers. In this respect, EPSs can be able to reduce sedimentation rate by increasing the product viscosity. In a yogurt-based Iranian drink, effects of addition of gellan at the percentages of 0.01, 0.03, and 0.05, alone as well as its combination with high-methoxy pectin at 0.25% on the quality characteristics of viscosity, particle-size, and serum separation were investigated. Gellan was effective against syneresis by forming strong networks, thus serum volume decreased. Moreover, sensory analysis performed after 1 day of storage at 5 °C indicated consumer acceptance of yogurt-based drink was not affected by addition of 0.05% gellan in the presence of high-methoxy pectin at 0.25% while stability of product was maintained [85].

11 Carrageenan

Carrageenan is one of the gel-forming and viscosifying EPSs, extracted from a number of seaweeds of the class Rhodophyceae. Carrageenan has a molecular mass above 100 kDa and is structurally sulfated polygalactan with 15–40% of ester-sulfate. Its structure contains D-galactose and 3,6-anhydro-galactose units and the units are linked by the glycosidic linkage of α-1,3 and β-1,4. Based on the sulfate content, there are different kind of carrageenans such as lambda (λ), kappa (κ), iota (ι), epsilon (ε), and mu (μ), changing 22–35% sulphate. Increase in ester sulfate content results in the decreasing solubility temperature and gel strength [124]. From a commercial perspective, iota (ι), kappa (κ), and lambda (λ) are important three main varieties of carrageenans. The κ-carrageenan is comprised of 3-linked β-D-galactose 4-sulfate and 4-linked 6-anhydro-α-galactopyranose which has one negative charge per disaccharide repeating unit while ι-carrageenan includes two sulfate groups per disaccharide repeating unit. In the medium containing cations such as K^+, Ca^{2+}, ι- and κ-carrageenans form highly viscous aqueous solutions, thus indicate gelling properties. However, λ-carrageenan is incapable to produce gel at all temperatures, and gelation of λ-carrageenan is feasible with trivalent ions [192].

EPSs have different functional properties and each has various application areas. Carrageenan is useful to produce gels in the presence of potassium and calcium ions in certain foods, i.e., meat products, dairy products, and desserts. Gelation of carrageenan has resulted from the helix formation that develops when a 3, 6 anhydro bridge is present on the B unit of the carrageenan molecule [71]. Three main forms of carrageenan including kappa, iota and lambda differentiate in the number of sulphate groups as one, two, and three per disaccharide in the structure, respectively. In an aqueous solution, ι- and κ-carrageenan change form from a temperature-dependent and disordered structure to ordered helix transition. The helix structure is related with the gelation property of the carrageenans [96]. Thus, the carrageenans are used mainly as gelling agents, but also as fat substitutes, stabilizing, and thickening agents in the food industry. Among three most important types of carrageenan, except trisulfated λ-carrageenan, only monosulfated κ-carrageenan and bisulfated ι-carrageenan are able to form gels. Hydrogels obtained by using κ-carrageenan have thermo-sensitive structural and thus, κ-carrageenan is preferred for developing delivery agents in which targeted compounds' release depends on the temperature. In encapsulation of active compounds such as antioxidants, enzymes, and probiotics, κ-carrageenan hydrogels have been used to protect compounds during production and storage of the food products [93].

Carrageenans are widely used in food industry for properties of gelling, thickening, and emulsifying. Carrageenans are added as texture enhancers or stabilizers in many types of food products like frozen desserts, sauces, ice cream, yogurt, chocolate milk, cheese, and meat products [18]. Synergistic effect of carrageenan with locust bean gum is applied in order to increase the gel strength and combination with other hydrocolloids have an effect on gel strength and cohesiveness. In dairy products, λ- and κ-carrageenan are commonly used to improve solubility and texture due to easy combination with milk proteins [124]. In the study performed by Günter et al. [64], gel microparticles were produced by using pectin and κ-carrageenan. Higher pectin concentration in the microparticle gels resulted in lower swelling degree in simulated gastric, intestinal, and colonic fluids. Addition of carrageenan into the gel formulation provided an increase in the swelling degree. Influence of the carrageenan types including iota, kappa, and lambda on the casein micelle and carrageenan interactions in milk were studied and all three types of carrageenan showed adsorption onto casein micelles. The most highly charged form of carrageenan was found as λ-carrageenan which indicates attractive interactions with casein micelles at the temperature of 60 °C [96]. Hydrocolloids have an important role in controlling ice recrystallization. The usage of κ-carrageenan as a secondary stabilizer was investigated in terms of stabilization of ice cream during storage [10]. It was indicated that κ-carrageenan significantly reduce the hardness and iciness and supported the functionality of primary stabilizer. κ-carrageenan was added to lactose-free frozen yogurts as a stabilizer with three different concentrations of 0.05, 0.1, and 0.15%. Quality characteristics of lactose-free frozen yogurts including acidity, texture, viscosity, overrun, melting properties, and color attributes were improved with 0.15% κ-carrageenan addition. Sensory properties were also better in the yogurt samples incorporated with κ-carrageenan [157]. Foerster et al. [53] studied on a milk emulsion system in order to determine the optimum amount of λ-carrageenan based on the size of fat globules and stability of emulsion. Emulsions prepared with a carrageenan concentration range of 0.3 and 0.4% indicated the highest stability and minimal fat globule size. Moreover, the addition of carrageenan into milk emulsions also provided stabilization and reduction of surface fat in powders obtained by spray drying. Thus, the λ-carrageenan is to be useful in powders of dairy-based emulsion by stabilizing emulsions in the presence of milk protein. In a viscous food model systems containing 10% of sucrose, the addition of λ-carrageenan was investigated in terms of the release of aroma compounds including aldehydes, esters, ketones, and alcohols. The difference between release of the aroma compounds in water and in viscous λ-carrageenan solution was compared by using dynamic headspace gas chromatography. Mass transfer of aroma compounds demonstrated a decrease in release rates was changed depending on the physicochemical characteristics of the aroma compounds, but the effect of λ-carrageenan on decreasing the release rates was observed in the most volatile compounds [18].

12 Hyaluronic Acid

Hyaluronan is glycosaminoglycan with a high molecular weight and it is formed from repetition of disaccharide units which comprise of D-glucuronic acid and D-N-acetylglucosamine linked by β-1,4 and β-1,3 glycosidic bonds. Dissachharide units found in the hyaluronan molecule changes in the number of 10000 or more. Synthesis of hyaluronic acid is provided by internal membrane proteins called as hyaluronan synthases [125]. Hyaluronic acid was discovered in 1934 and its extraction was obtained from animal tissue, especially from rooster coombs. However, now production of hyaluronic acid is performed by recombinant bacteria [121].

Hyaluronic acid has a role as key molecule in the regulation of various cellular and biological processes. Thus, hyaluronic acid has been used for many biomedical applications not only due to the biocompatible, biodegradable, and nonimmunogenic properties but also because of its biological functions [136]. Synthesis of hyaluronic acid is occurred by many *Streptococcus* species such as *Streptococcus equi, Streptococcus equisimilis*, *Streptococcus pyogenes.* Among the species, *S. equi* subsp. *zooepidemicus* achieved industrial production of hyaluronic acid, but these strains are known as pathogenic. Therefore, a recombinant strain of *Bacillus subtilis* was found to be able to produce hyaluronic acid on a laboratory scale [74]. Recently, *S. thermophilus* isolated from traditional dairy food products was investigated for production of hyaluronic acid. It was found to be effective to produce EPSs including hyaluronic acid with a wide range of molecular masses [74]. Hyaluronic acid is found to be useful natural material in surgery of human eye due to the compatibility with human immune system. Another property of the hyaluronic acid which makes it useful is high water-binding capacity. The water-binding capacity of hyaluronic acid was remarked as up to 6 litres of water per gram of the polysaccharide, that associated with molecular mass of the polysaccharide [163].

Hyaluronic acid is mainly used as a hydrating agent in cosmetics and pharmaceuticals, and also used in eye surgery due to its biological properties [163]. The usage of hyaluronic acid in food industry is limited. Hyaluronic acid is also known with the ability to form biocompatible films or hydrogels in defined conditions. Galactomannans are a kind of polysaccharides used to increase the viscosity of food products and in films/coatings for foods. Combination of galactomannan and hyaluronic acid was investigated in order to observe physical and chemical characteristics of hyaluronic acid in solution. Two types of galactomannans including guar gum and locust bean gum improved the viscoelastic behavior in hyaluronic acid mixture solution compared to pure solution. Synergism between hyaluronic acid and locust bean gum was obtained successfully at 50% in which hydrogel with the best viscoelastic behavior and desired properties was obtained [112]. Nano-delivery system based on oligo-hyaluronic acid and loaded with curcumin and resveratrol was produced successfully and the hyalurosomes containing both curcumin and resveratrol were suggested to improve stability, bioavailability, and antioxidant activity of functional compounds used into juice, yogurt, and nutritional supplements. Coencapsulation of curcumin and resveratrol in hyalurosomes formulation was obtained with the average particle nano-size of 134.5 ± 5.1 nm and stability observed in vitro gastrointestinal release test [65]. In another study, caffeic acid as an antioxidant agent was incorporated into biopolymer hydrogels composed of hyaluronic acid, hydrolyzed collagen, and chitosan. Increase in the amount of hyaluronic acid resulted in excellent swelling behavior. Release of caffeic acid in the produced hydrogels was initially 70% within 60 min and followed by a release of 80% in 480 min [30].

13 Levan

Levan is a homopolysaccharide comprised of fructose, which makes it a unique carbohydrate. A wide range of microorganisms are capable to produce levan as an exopolysaccharide while limited plant-based sources are found to be the storage of levan. Bacterial strains producing levansucrase include *Lactobacillus johnsonii* and *Lactobacillus gasserii*, *Bacillus subtilis, Aerobacter levanicum, S. salivarius*, etc. Levansucrase plays a part in catalysation of the transferring D-fructosyl residues from fructose to yield levan. Thus, levansucrase is a catalyzer of microbial levan biosynthesis [159]. Among the bacteria, *Bacillus subtilis* Takahashi is known as the most efficient strain in terms of levan production. Structurally, levan is a fructose polymer including β-(2, 6)-linkages and also about 12% branched with β-(1, 2)-linkages. Its molecular weight is around 2×10^6 Da [169]. Levan can differ from the molecular weight and the fraction of residues incorporated in side chains according to the source obtained and conditions produced. It is an exopolysaccharide with a variety of usage in cosmetics, foods, and pharmaceuticals [1]. In terms of solubility, levan is a water-soluble carbohydrate polymer, but insoluble in all organic solvents like methanol, ethanol, isopropanol, n-propanol, acetone, toluene, etc. [159]. Intrinsic viscosity of levan is lower than other polysaccharides having similar molecular weight. Its low intrinsic viscosity is affiliated with the compact and spherical molecular conformation of the polysaccharide. Intrinsic viscosity values for levan in water was found in a range of 0.07 and 0.18 dL/g [6].

Levan is an exopolysaccharide used with a variety of usage in cosmetics, foods, and pharmaceuticals. Potential applications of levan have been mentioned as an emulsifier, stabilizer, thickener, encapsulating agent, and carrier for flavors. In addition, it is found efficient in inhibiting hyperglycemia and oxidative stress induced by diabetes [36]. Rheological properties of the solutions of levan obtained from *Bacillus* spp. were investigated at 20 °C and different concentrations. The intrinsic viscosity of obtained levan was compared with the levans produced by other bacteria. Viscosity values demonstrated shear-thinning behavior appears at a higher concentration than for other levans [6]. Levan has been used in the production of nanostructured system. Encapsulation of nanoparticles incorporated with vitamin E was performed by using levan and effect of parameters such as type of homogenization, speed of homogenization, and concentration of vitamin E on encapsulation efficiency was investigated. In the study, nanoparticules having spherical particles between 50 and 100 nm were successfully produced by homogenizer at the conditions of 16000 rpm speed and vitamin E concentrations ranging from 2 to 10% [40].

14 Colanic Acid

Colanic acid is an important exopolysachharide in terms of the survival of *E. coli* for outside the host. Fundamentally, lipopolysaccharides produced by Gram-negative bacteria includes O antigen which is a polysaccharide component. Antigens including total of 173 O, 80 capsular, and K antigens are determined in *Escherichia coli*. Among these antigens, colanic acid, in other words M antigen, is widely found exopolysaccharide produced by *E. coli* and also other species of Enterobacteriaceae family [160]. Colanic acid is found as a major component in sugar composition of EPSs obtained from isolated bacteria including *Enterobacter* sp., *Klebsiella* sp., *Enterobacter amnigenus, Citrobacter* sp., *Enterobacter cloacae* [138]. Different factors based on genetic and environmental conditions such as membrane integrity, cell envelope stress, osmotic shock, metabolic stress, growth pH, or temperature are determined to activate the synthesis of colanic acid in cells [175].

Colanic acid is important forms of EPSs located on the cell surface of *Escherichia coli*, *Shigella* spp., *Salmonella* spp. and *Enterobacter* spp. In the literature, any information has not been found in the applications in food products. Applications of colanic acid are mentioned in cosmetics and personal care products with its gelling property [132].

15 Welan

Welan is an exopolysaccharide produced by *Sphingomonas* sp. which is also known as *Alcaligenes* sp. and gram-negative bacteria. The production of welan is carried out by submerged fermentation from *Alcaligenes* species and using a medium including glucose, ammonium nitrate, di-potassium hydrogen phosphate, magnesium sulphate, and ferrous ions. The yield of welan depends on the factors such as source of carbon, source of nitrogen, temperature, agitation speed, pH, and others [83]. Welan and gelan have similar structures with same repeating unit. However, welan has a single glycosyl side-chain substituent that can be an a-L-rhamnopyranosyl or an a-L-mannopyranosyl unit linked (1 → 3) to the 4-O-substituted β-D-glucopyranosyl unit in the main structure [81].

Welan is well known with its high viscosity even at very low concentrations and its high viscosity retained stable at high temperatures for long time. For instance, compared to xanthan which is another thermostable polysaccharide, while viscosity of xanthan solutions disappear at 135 °C, viscosity of welan solutions maintained up to 163 °C [81]. Rheological properties of welan solutions were explained in fresh water, sea water, and 3% KC1 solutions. The rheological properties obtained by welan ensure higher penetration rates, lower formation damage, and good suspensions as an advantage. It has also an important role to prevent phase separation in cementitious products. Welan gum has been used as thickening, binding, or emulsifying agent in food products such as jellies, beverages like citric acid based drinks, dairy products like ice creams, yogurt, and salad dressings [83]. However, in the literature, studies focused on the rheological properties of welan gum solutions and applications in food products were limited. Effect of welan gum addition on viscoelastic properties, flow behavior, droplet size distribution, and physical stability of thyme oil in water emulsions was investigated by Martin-Piñero et al. [111]. While emulsion without welan gum indicated Newtonian behavior, emulsions including welan gum showed a weak gel-like behavior with greater viscosity. It was pointed out that welan gum played an important role as a rheological modifier for thyme oil in water emulsions. Thus, it is a natural polysaccharide which can control the rheological properties of these kinds of emulsions by Martin-Piñero et al. [111] (Table 1).

16 Conclusion

The microbial polysaccharides can open up new opportunities in the food industry that are environmentally friendly, sustainable, and multifunctional. Microbial EPS are used in the food industry due to their unique characteristics such as emulsifier, stabilizer, thickener, texturizer, encapsulating and carrying of bioactive agents, and coating and film-forming ability. Microbial EPSs have the potential to be utilized as food additives and functional food ingredients. Microbial EPSs structural complexity, low production yield, and production cost are the most critical challenges for microbial polysaccharides utilization in the near future; however, agro-industrial wastes could be considered as an alternative for reducing the microbial polysaccharides production cost. The new microbial EPSs engineered structures with multifunctional properties have the potential to broaden the food applications. Considering the utilization of microbial EPSs as the introduction of green technology in the food industry offers great potential for clean label products and promotes health benefits.

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