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A Review of Current and Future Food Applications of Natural Hydrocolloids

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Summary

The main aim of this review paper is to focus on current and potential future sources and food applications of natural hydrocolloids in the food industry. The emerging research trends, problems, new methods, and alternative approaches in production, environmental concerns, market trends, and newly discovered health benefits have been discussed for natural hydrocolloids of commercial relevance. The rheological and surface active properties, interactions, functional properties, films and coatings, encapsulation applications, as well as nanotechnology uses of natural hydrocolloids have been discussed in the light of recent developments. This review also reflected the most up-to-date concepts of applying natural hydrocolloids to meet consumer's and food sector's sophisticated demands related to food products.

Key words: Natural hydrocolloids, food applications, functional properties, packaging, encapsulation, nanotechnology, health benefits

Introduction

In recent years, natural hydrocolloids have been increasingly used in the food industry to improve stability, functional properties, quality and safety, and nutritional and health benefits of different food products such as beverages, bakery and confectionary, sauces and dressings, meat and poultry, etc. Various market reports and forecasts suggest that the global food hydrocolloids market will increase in value by minimum 50% within the next ten years. Thus, extensive efforts are needed to improve productivity of current hydrocolloid sources and to evaluate different agro-industrial wastes as source of hydrocolloids. The most conventional applications of hydrocolloids in the food industry are still those based on their

functional properties, mainly rheological and surface active properties (Nishinari *et al.*, 2018; Yousefi and Jafari, 2019). The use of hydrocolloids in the encapsulation of food additives, bioactive compounds, prebiotics and probiotics, and nutrients has also become a dynamic field. Moreover, hydrocolloids are used as edible coatings not only on food to improve their safety, quality and functionality (Tiwari, 2017), but also on coating of plastic films in order to improve their functional properties. On the other hand, the application of hydrocolloids in nanotechnology to develop novel packaging and encapsulation technologies is an emerging field that provides unique technological attributes that could not be achieved with classical methods (Bajpai *et al.*, 2018). Another emerging application of food hydrocolloids involves their use to improve health benefits and nutritive value of food. Due to their prebiotic activity and/or effects on metabolic and chronic diseases, hydrocolloids, such as pectin, inulin, β -glucan, resistant starch, etc., have been extensively used in food formulations with health claims (Viebke *et al.*, 2014). The main aim of this review paper is to focus on current and potential future sources and food applications of hydrocolloids in the food industry. A particular emphasis was paid to emerging research trends, methods and market trends that shape the future sources, increase technological and health benefits, and bring a new insight into conventional uses of hydrocolloids.

Current and Future Sources of Hydrocolloids and Related New Trends

Hydrocolloids from plant sources. The nanofibrillated cellulose and microcrystalline cellulose (MCC) obtained by physical modification of cellulose, and different chemically modified derivatives of cellulose (cellulose ethers), such as carboxymethyl cellulose (CMC), methylcellulose (MC), hydroxypropyl methylcellulose (HPMC) and hydroxyethyl cellulose (HEC), have been extensively used in the food products. However, the sodium salt of CMC is the major derivative used by the food industry. Cellulose is generally obtained from wood, but some non-wood based plant sources (such as

cotton fibre, pea hull fibre, ramie fibre, banana fibre, sisal fiber, kenaf pulp, and flax fibre), bacteria, algae and marine tunicates could also be used in cellulose production (Thakur and Thakur, 2014).

Native starches and modified starches are also a major group of food hydrocolloids. The functional properties (gel properties: texture, gelling time and temperature, heat resistance, etc.) of native starches differ depending on their granule size and amylose/amylopectin ratios. The type of starch also affects the health benefits of final food products. For example, corn, rice, potato and tapioca starches are used in place of wheat starch in foods designed for people suffering from gluten intolerance or celiac disease. However, modifications and new technological processes are needed to improve the baking and the bread making quality of wheat alternative starches (Yano *et al.*, 2017). The physical and chemical starch modifications have been applied extensively: *i*) to improve starch stability and functionality; *ii*) to reduce the retrogradation of starch during processing; or *iii*) to obtain resistant starches that help struggling with obesity and related diseases. On the other hand, enzymatic hydrolysis of native starch with amylases is applied to obtain sweeteners such as dextroses and maltodextrins.

Pectin obtained from citrus peels and apple pomace is another primary food hydrocolloid. Major industrial pectin forms are high-methyl ester pectin (HMP) (degree of esterification (DE): >50%), and pectins obtained by HMP modification such as low-methyl ester pectin (LMP) (DE: <50%) and amidated low-methyl ester pectin. Due to the huge demand in thickening and gelling agents, alternative sources such as sun-flower heads and sugar beet pulp have also been used in pectin production. Moreover, a significant interest exists to employ environmentally friendly and mild pectin extraction methods (e.g. microwave, ultrasound or enzyme assisted extractions) in place of classical hot acidic extraction (Marić *et al.*, 2018). The enzymatic, thermal, and chemical modification of pectin

is also an emerging field since modified pectins with improved health benefits can be used in functional and medical foods, and nutraceuticals (Bernardino *et al.*, 2019).

Due to both the health concerns related to food of animal origin, and the related growing demand in vegan food, soy proteins (e.g., concentrates, isolates, and texturized forms) are extensively used in food formulations. Soy proteins are not only highly functional, but they also provide all of the nine essential amino acids as well as bioactive isoflavones. Thus, FDA approved use of soy protein with 2 different health claims (FDA, 2018). However, due to both the problems posed by genetically modified organisms (GMOs) and the allergens associated with soy proteins, production and use of soy-alternative plant proteins, such as pea and potato protein isolates, have been increased. Moreover, the use of hemp protein isolate by vegetarians has also boosted since it does not contain allergenic factors (Mamone *et al.*, 2019).

Gums derived from different plants (e.g., guar bean gum, locust bean gum, karaya gum of *Sterculia urens* tree, gum tragacanth from stems and branches of Asiatic species of *Astragalus*, and gum Arabic from different species of acacia tree) are also used by the food industry, mainly for their thickening properties.

Hydrocolloids from animal sources. Gelatin obtained from partial hydrolysis of collagen in pigskin, and in bovine cartilage, bones and hides is the major animal protein used for its unique gelation and foaming capacity, elasticity, texture, taste and nutritive value. However, due to the religious and health concerns associated with mammalian gelatins (risk of spreading prions with bovine gelatins), there is a significant industrial interest in use of gelatin obtained from by-products of the fishery industry. In general, gelatin of warm water fish shows gelation properties (gel strength and setting/melting temperatures) that are comparable with those of mammalian gelatin. However; the gelation properties of gelatin from cold water fish which represents the majority of the industrial fisheries are inferior than

those of mammalian gelatin (Benjakul and Kittiphattanabawon, 2019; Alfaro *et al.*, 2015). Moreover, it is suggested that by-products of low-allergy fish (e.g., tuna) should be evaluated in gelatin production to minimize the risk of fish allergy (André *et al.*, 2003). On the other hand, gelatin from poultry (chicken and turkey) processing wastes (e.g. skin, feet and bone) might be an important source of gelatin in the future since it is free from major religious concerns and health risks.

Due to their unique binding (pasting), emulsification and coagulation properties as well as the excellent nutritional value, proteins from whole eggs, egg yolk and white (albumen) are extensively used by the food industry (in fresh, pasteurized, dried or frozen form). Different proteins or fractions of yolk (e.g., granules proteins, lipidic paste protein, plasma) have great potential as alternative gelling and emulsifying agents (Laca *et al.*, 2010; Valverde *et al.*, 2016). The purified egg white proteins, such as ovalbumin (excellent source of amino acids), ovotransferrin and phosvitin (antioxidant and antimicrobial), and lysozyme (antimicrobial), also have good potential as food additives (Huopalahti *et al.*, 2007).

Whey protein concentrates (WPC) and isolates (WPI) obtained as a by-product of cheese-making, and caseinates obtained from skim milk with classical acidic precipitation are among the most commercially important hydrocolloids. The development of membrane separation methods such as ultrafiltration, microfiltration, and diafiltration have also increased the use of micellar casein concentrates, and milk protein concentrates and isolates (containing both casein and whey proteins) obtained from skim milk (Crowley *et al.*, 2018). The demand for milk proteins has been increasing because food industry prefers to use milk proteins in emerging high-protein foods.

Chitosan (CHI) produced mainly by alkali deacetylation of chitin extracted from shells of crustaceans, a by-product of fishery industry, is another animal source hydrocolloid. Due to its inherent antibacterial and antifungal properties, the food industry uses chitosan mainly as

an antimicrobial film or coating material (van den Broek et al., 2015). Moreover, use of chitosan as a nanoencapsulant for bioactive substances and nutrients has increased since it brings different advantages (e.g., controlled release, bioavailability, stability etc.) (Akbari-Alavijeh et al., 2019).

Hydrocolloids from seaweed. Agar and carrageenans (kappa-, lambda- and iota-) produced by red seaweeds (*Rhodophyceae*) and alginate obtained from brown seaweeds (*Phaeophyceae*) are the main marine origin food hydrocolloids. Alginate is produced mainly as Na-alginate from alginophytes, such as *Ascophyllum nodosum* and *Laminaria digitate*. The only modified commercial alginate form is propylene glycol alginate. On the other hand, agar is extracted from agarophytes such as *Gelidium corneum* and *Gracilaria spp.* while carrageenan is produced mainly from carrageenophytes such as *Kappaphycus alvarezii* and *Euचेuma denticulatum* (Fleurence and Levine, 2016; Porse and Rudolph, 2017). The hottest research topics in the field of seaweed hydrocolloids are application of the resource management (Santos and Melo, 2018), and sustainable and green methods in seaweed cultivation and processing (Porse and Rudolph, 2017). Moreover, there is an interest in production of bioactive polysaccharides from seaweeds, such as laminarin, a β -glucan obtained from brown algae (Kadam et al., 2014).

Hydrocolloids from microorganisms. Major microbial food hydrocolloids include fungal polysaccharides such as pullulan from *Aureobasidium pullulans* and bacterial exopolysaccharides (EPS) such as xanthan from *Xanthomonas campestris*, gellan from *Pseudomonas elodea*, and cellulose from *Komagataeibacter xylinus* and *Acetobacter xylinum*. Extensive studies are also continuing to improve viscosity, texture and mouthfeel of dairy and bakery products, and water absorption capacity and textural properties of meat products by using EPS producing lactic acid bacteria in their fermentation (Oluk et al., 2013; Lynch et al., 2018; Hilbig et al., 2019).

Rheological Properties of Natural Hydrocolloids

Hydrocolloids are widely used to thicken food systems and as gelling agents. The viscosity of hydrocolloid polymer solutions shows a marked increase at a critical polymer concentration (C^*), in correspondence of which the transition from the 'dilute region' (i.e., the polymer molecules are free to move independently in solution without interpenetration), to the 'semi-dilute region' (i.e., where molecular crowding gives rise to the overlap of polymer coils and interpenetration) occurs. Solutions of most polysaccharide hydrocolloid have Newtonian behavior (viscosity does not depend on the rate of shear) at concentrations well below C^* . However, for concentrations above C^* viscosity is no longer independent from the shear rate, and a non-Newtonian behavior is observed.

The relationship between viscosity and shear rate for a hydrocolloid polymer solution for concentrations above C^* is schematically displayed in Figure 1. The first region (a) is named low-shear Newtonian plateau and represents an initial state when no shear is applied. At this moment, some molecules can have a certain degree of entanglement and arrange in a spherical organization, while others are less organized and partially disentangled. As soon as a low shear is applied, molecules approach each other giving rise to collisions that contribute to increase the viscosity. At the same time, a counterbalancing effect is due to the partial disentanglement of entangled molecular chains, which orient in the shear direction, thereby decreasing the viscosity. Overall, the viscosity of the system remains the same. The second region (b) is a shear-thinning region. In this region, with the increase of the shear rate, disentanglement and orientation prevail entanglement of molecules, with an overall decrease of the viscosity. The third region (c) is a high-shear Newtonian plateau, where the viscosity does not change further because of the orientation of molecular chain has reached its maximum (Khatibi *et al.* 2016).

There are three major parameters having significant effects on the viscosity of polymer solutions. The first parameter is the molecular mass of a polymer. The viscosity dependency on the shear rate increases with increasing molecular mass; concurrently, the shear rate at which shear thinning occurs shifts to lower values for higher molecular masses. The second major parameter is the hydrodynamic size. Linear and stiff molecules give solutions with much higher viscosity than highly branched, highly flexible polymers of the same molecular mass because of a larger hydrodynamic size. Cellulose and its derivatives (e.g., CMC and HEC) are stiff molecules with a typical linear structure; they exhibit a shear thinning behavior, with a high viscosity at low shear rates that decreases with increasing shear. Conversely, flexible hydrocolloids such as pullulan and dextran (flexibility originates from α -(1 \rightarrow 6) glycosidic linkages), and gum Arabic (flexibility originates from its highly branched structure) have relatively small radii of gyration for their molecular mass compared to the linear cellulosic polymers. Interpenetration only occurs to a limited extent even at concentrations of 20–30%, which explains their Newtonian characteristics. The third major parameter is the charges of polymers. The presence of charged functional groups on the backbone of the polymer yields solutions with a higher viscosity than solutions made of non-ionic polymers of similar molecular mass. The main reason is that charged polymers have a more expanded arrangement in solution due to intramolecular charge repulsions. A significant drop in viscosity can be induced by adjusting either the pH or the ionic strength of the solution, which would promote aggregation of the polymer chains by reducing the degree of dissociation of the charged groups (Akbari *et al.*, 2019; Tengku Mohd *et al.*, 2018).

The gelation is another important rheological property of hydrocolloids. Hydrocolloid solutions are viscoelastic and, above C^* , the formation of a three-dimensional network (i.e., a gel) occurs due to entanglement between molecular chains leads. Because the junction zones of the three-dimensional network are given by physical interactions (e.g., hydrogen bonding,

hydrophobic association, electrostatic crosslinking, etc.), hydrocolloid gels are referred to as 'physical' gels (also called 'reversible' or 'pseudo' gels) (Hoffman, 2002) and differ from 'chemical' gels (also called 'irreversible' or 'permanent' gels) (Hoare and Kohane, 2008) which normally consist of covalently cross-linked polymer chains (Farris *et al.*, 2009a; Farris *et al.*, 2011a). Some hydrocolloids form gels due to changes in temperature (cooling or heating) and they usually are denoted as thermo-reversible gels. Non thermo-reversible gels are nearly insensitive to changes in temperature, and their gelation can be driven mostly by divalent cations (e.g. Calcium atoms in the case of negatively charged hydrocolloids such as low-methoxy pectins and alginates). Gel formation occurs above a critical minimum concentration, which is specific for each hydrocolloid. Agarose, for example, will form gels at concentrations as low as 0.2%, while for acid-thinned starch, a concentration of ~15% is required (Phillips and Williams, 2000).

Surface Active Properties of Natural Hydrocolloids

Food hydrocolloids owe their surface active properties mainly to their amphiphilic nature that causes their rapid adsorption by oil-water or gas (e.g. air, nitrogen or carbon dioxide)-water interface to form emulsions (oil-in-water) and foams, respectively. Proteins have an inherent amphiphilic nature originating from their building blocks, the amino acids, that contain hydrophilic, hydrophobic or amphiphilic R groups. In general, compact and globular proteins cannot form desired emulsions and foams because of their rigid tertiary structure that hinders rapid unfolding and formation of an interfacial film. In contrast, non-globular and flexible proteins, because of their hydrophilic and hydrophobic groups or domains exposed to the medium, can be readily adsorbed to an interface, unfold and reorient at the interface, and form a strong cohesive and viscoelastic interfacial film that is stable to thermal and mechanical shocks (Damodaran, 1996). In an oil-in-water emulsion (O/W) the hydrophilic residues or domains of a flexible protein interact with the aqueous phase of the

oil-water interfaces. In contrast, the hydrophobic parts of protein interact with the oil phase of oil-water interfaces to form a cohesive viscoelastic film around the dispersed oil droplets, hence preventing their coalescence by either steric hindrance or electrostatic repulsions (the latter depending on the pH of the emulsion). The non-micellar caseins such as Na-casinate, and whey protein found in whey protein concentrates are good examples of surface active hydrocolloids (McSweeney, 2008). In contrast, micellar caseins found in milk protein concentrates show poor surface active properties since calcium bridges found among submicelles prevent their unfolding and orientation at interfaces (McSweeney, 2008). On the other hand, most of the polysaccharides show mainly a hydrophilic character, and they cannot be classified as surface active agents. However, some polysaccharide-based hydrocolloids such as soluble soybean polysaccharide (SSPS), gum Arabic, and sugar beet pectin that contain a complex hydrophobic protein component, and polysaccharides chemically incorporated with hydrophobic groups (e.g. HPMC, HPC and octenyl succinic anhydride modified starches) could participate in formation and/or stabilization of emulsions.

Interactions of Hydrocolloids and Related New Trends

Hydrocolloids and most of food components are chemically reactive or at least contain various reactive groups (e.g. $-\text{SH}$, $-\text{S}-\text{S}$, $-\text{NH}_2$ and $-\text{NH}-\text{C}(=\text{NH})\text{NH}_2$ in proteins, peptides and amino acids, and $-\text{OH}$, $-\text{CHO}$ and $\text{R}_2\text{C}=\text{O}$ in proteins and carbohydrates) (Sikarski *et al.*, 2007). Therefore, hydrocolloids added into food as functional agents could interact with each other or with different food components (Table 1). The interactions formed with food components such as water, proteins, carbohydrates, lipids, organic acids, minerals, flavor compounds, polyphenols, carotenoids, etc. affect not only the functional properties of hydrocolloids, but also a number of quality attributes (e.g., color, texture, and flavor), stability, health benefits, and nutritional value of foods. The interactions of protein hydrocolloids with food components such as tannins, carbonyls and lipid peroxides lead to

the reduction in their nutritional value while the interactions between protein hydrocolloids with food components such as water, proteins, polysaccharides, lipids, and minerals lead to changes in their functional properties such as hydration, solubility, viscosity, film formation, and gelation (Gao *et al.*, 2017). Similarly, the interactions of polysaccharide-based hydrocolloids with different food components result in change of their functional properties such as viscosity, gel setting rate, and gel rheology (Sikarski *et al.*, 2007).

A recent emerging trend in the use of hydrocolloids is that interactions between compatible hydrocolloids or between hydrocolloids and food components are exploited to achieve novel functional, structural, and textural properties in the food systems (Gao *et al.*, 2017). For example, acidified milk products containing combination of CMC and HMP gave more stable products with better rheological and mouthfeel properties than those with CMC employed frequently alone to prevent serum separation in these products (Yuliarti *et al.*, 2019). Moreover, gelatin-pectin electrostatic complexes having similar textural properties with starch paste could be employed in place of starch to develop reduced-calorie food (Wu *et al.*, 2014). Similarly, egg white protein could be combined with different gums (guar, locust bean, xanthan, and karaya gums) to obtain gels having different mechanical and textural properties and water holding capacity (Khemakhem *et al.*, 2019). Furthermore, interactions (ionic and H-bonding) of gluten and starch in dough with different nonionic (guar gum, locust bean gum) and anionic (alginate, pectin, carrageenan, xanthan gum) hydrocolloids could be exploited to improve rheological, pasting or fermentation behaviors of the dough (Li *et al.*, 2019). Tan *et al.*, (2018) successfully employed this strategy with hydrocolloids such as xanthan, carrageenan or locust bean gum to improve water holding capacity of dough, and increase quality (e.g. cooking yield and firmness) of obtained cooked salt free noodles. It is expected that these and many similar studies will continue to expand the industrial applications of hydrocolloids.

Interactions between hydrocolloids and food components are discussed in detail in previous review papers (Gao *et al.*, 2017; Lv *et al.*, 2017). In particular, the interaction between hydrocolloids and polyphenols is receiving a great deal of attention because of the central role polyphenols in emerging functional foods and biopreservatives market. In general, the interaction of protein-based hydrocolloids with polyphenols occurs via H-bonding (formed between –OH groups of polyphenols and peptide carbonyl groups of protein) and hydrophobic interactions (Bandyopadhyay *et al.*, 2012). On the other hand, the polar groups (e.g. acetal, hydroxyl or carboxyl) of polysaccharide-based hydrocolloids interact and bind phenolic –OH groups with H-bonds and van der Waals forces (Wu *et al.*, 2009; Palafox-Carlos *et al.*, 2011). Hydrocolloids might also form some ionic interactions with polyphenols. For example, electrostatic interactions can take place between flavylum cation of anthocyanins and dissociated carboxylic groups of hydrocolloids (Belitz and Grosch, 1999). The hydrocolloid-polyphenol interaction not only affects the functional properties of hydrocolloids, but also causes significant changes in stability, bioavailability, and bioactivity of polyphenols (Palafox-Carlos *et al.*, 2011; Jakobek and Matic, 2018) (Table 2). Thus, the positive and negative effects of hydrocolloid-polyphenol interactions should be carefully evaluated during application of hydrocolloids.

Hydrocolloids as Functional Agents

The functional properties of protein and polysaccharide hydrocolloids exploited in the food industry originate from their capacity to improve viscosity or thickness, to cause gelation, texturization, suspension, stabilization, emulsification, foaming, cohesion-adhesion, water binding, oil and flavor binding, or to prevent ice-crystal formation, sugar crystallization, drip-loss, serum separation etc. (Saha and Bhattacharya, 2010; Damodaran and Paraf, 1997) (Table 3). Natural polysaccharides are used in the food industry mainly as thickening agents (e.g., starches, celluloses, xanthan, guar gum, locust bean gum, gum

karaya, gum tragacanth, and gum Arabic) and gelling agents (e.g., alginate, pectin, carrageenan, gellan, and agar) (Saha and Bhattacharya, 2010). Although the majority of polysaccharides are not good surface active agents, they could also stabilize the emulsions by different mechanisms. For example, polysaccharides could delay coalescence of the lipid globules by thickening of the aqueous phase surrounding the oil globules and/or forming layers of association structures (a liquid crystal layer) at the aqueous phase surrounding the lipid globules (Milani and Maleki, 2012). Moreover, some carbohydrates (e.g. nanoparticles of chitosan and cyclodextrin microcrystals) could form Pickering emulsions by forming particles locating at oil-water interface, thereby preventing coalescence of oil droplets (Yang et al., 2017). On the other hand, proteins are used extensively for their multiple functional properties originating from their rheological and surface active properties, texturization, gelation, water, oil or flavor binding properties etc. (Damodaran, 1996). Some hydrocolloids are indispensable both with their worldwide economic importance and unique functional properties. For example, the mammalian gelatin is indispensable because of its unique ability to form gels that melt at body temperature and release flavors in the mouth. Similarly, eggs are major poultry products that contain proteins having excellent nutritional properties and unique binding (pasting), coagulation, foaming and emulsification properties that make them almost indispensable for desserts, confectionery and bakery products, pasta, ect. (Valverde *et al.*, 2016). Emulsification properties of caseinates and soy proteins; thickening properties of starches, celluloses, and their derivatives without affecting odor and taste of food; thermo-irreversible cold-setting gel formation capacity of HMP at low-pH and high sugar concentration; and heat-stable and cold-formed gels of alginates induced by calcium ions are all highly desired functional properties that cause worldwide use of these hydrocolloids.

Hydrocolloids as Packaging Materials

At the beginning of the 1990s of the last century, the use of hydrocolloids for the fabrication of edible films and coatings was proposed (Krochta *et al.*, 1994; Guilbert *et al.*, 1996). Since then, fervid, seemingly never-ending research activities related to the use of protein and carbohydrate source hydrocolloids in the formulation of edible films have been conducted worldwide. The edible coatings have long been used to provide natural casing materials for meat products (e.g. small or large intestines of cattle and sheep used for sausages), to delay respiration rate and moisture loss of fruits (e.g. cellulose derivatives, casein, zein, soy protein, chitosan), and to prevent diffusion of moisture and oxygen into nuts (e.g. whey protein, zein) (Yemenicioglu, 2017). The use of edible films to isolate different food layers from each other, to stick and adhere different food components or to increase the structural integrity of food formulations are also typical applications extensively used by the food industry. On the other hand, the use of edible coatings in active packaging created a huge potential to boost novel uses of food hydrocolloids (Tiwari, 2017). Active edible coating is an emerging method that might (1) increase the microbial safety or delay the microbial spoilage of food (antimicrobial packaging); (2) control oxidative changes in food (antioxidant packaging); or (3) deliver nutrients or bioactive substances onto food surface in bioavailable form (bioactive packaging) (Yemenicioğlu, 2017). The use of nanoparticles in active edible coating attracts a significant interest from researchers since this provides unique film properties (e.g. mechanical and gas barrier properties), and antimicrobial and controlled release properties for the active agents (Zambrano-Zaragoza *et al.*, 2018; Xing *et al.*, 2019).

Although edible food coatings have found practical use in a large number of market applications, the possibility of using hydrocolloids to generate self-standing biopolymer films, possibly to replace conventional plastics, is restricted to laboratory experiments. For example, different studies exist to obtain edible self-standing films from polysaccharides (e.g.

chitosan, starch and pectin) and proteins (e.g. zein, collagen, soy protein, wheat and corn gluten, whey protein, casein, gelatin) by using polymer processing methods such as extrusion, extrusion blowing, injection molding or compression molding (Verbeek and van den Berg, 2010; Espitia *et al.*, 2014; Oechsle *et al.*, 2016; Sam *et al.*, 2016). However, technical hurdles linked to both processing operations and performance heavily hinder translation of hydrocolloid based edible materials into next-generation packaging materials at an industrial scale. On the one hand, hydrocolloids must be processed differently from polymers of fossil origin. For example, extrusion could never take place in conventional extrusion plants due to the severe processing conditions in terms of, e.g., thermal and shear stresses. Consequently, specific manufacturing lines should be designed for the production of biopolymer films based on hydrocolloids. On the other hand, films obtained from hydrocolloids exhibit physicochemical properties that make them unsuitable for food packaging applications. For example, poor mechanical properties, high sensitivity to moisture, and inadequate thermal stability dramatically affect the structural and functional integrity of most films based on hydrocolloids (Wu *et al.*, 2013; Wu *et al.*, 2015; Wu *et al.*, 2018 Arcan and Yemenicioğlu, 2011).

At the beginning of the new century, the use of thin layers of hydrocolloids coated on conventional food packaging materials has been proposed, in particular plastics and, to a lesser extent, cellulose and its derivatives. The inspiring principle was the possibility of exploiting some specific features of biopolymers to reduce the amount of petrol-based polymers required (e.g., polyvinyl alcohol [PVOH], ethylene vinyl alcohol [EVOH], and polyvinylidene chloride [PVDC]), thus meeting the increasing need for environmental sustainability. Over the years, several works have demonstrated the great potential of hydrocolloids to act as a functional coating in order to improve one (or even more) specific property of the substrate (Table 4).

Early research has focused on what is probably the most important feature of hydrocolloids: their excellent performance as a barrier against oxygen permeation. This property is mainly due to the extensive hydrogen bond formation at the intermolecular level between hydroxyl and amino groups, with a subsequent increase in network density. However, this performance is found with relative humidity (RH) values $\leq 50\%$, above which an exponential increase of the permeability is observed due to the detrimental effect of water molecules on the biopolymer network's stability. For this reason, biopolymer coatings are well suited as high-oxygen-barrier layers if they are sandwiched between two moisture-barrier films (e.g., two polyolefins). Alternatively, strategies to improve the oxygen-barrier performance of biopolymer coatings at high-RH conditions include the addition of a hydrophobic component to coating formulations (Farris *et al.*, 2009b) as well as more sophisticated approaches, such as bottom-up and top-down nanotechnology routes (Farris *et al.*, 2012; Introzzi *et al.*, 2012a; Svagan *et al.*, 2012; Fuentes-Alventosa *et al.*, 2013; Unalan *et al.*, 2016; Unalan *et al.*, 2017). Hydrocolloids have also been used as a sealing coating, to replace the so-called cold sealant used for specific classes of foods such as ice creams, baby foods, and chocolate-based snacks (Farris *et al.*, 2009c). For example, gelatin can be used to generate coatings with tunable sealing attributes, i.e., from peelable to high-strength, using a sealing temperature ranging from 50 °C to 90 °C (Farris *et al.*, 2010). Gelatin coatings have been also demonstrated to be effective barriers against UV radiation (Farris *et al.*, 2009b), attributable to the aromatic amino acids in the gelatin composition, like phenylalanine and tyrosine. This UV-absorbing behavior becomes especially relevant when using polyolefins, which are very transparent to UV radiation.

Hydrocolloids have also been used as surface modifiers of plastic webs (Farris *et al.*, 2011b). Due to their inherent hydrophilicity, biopolymer coatings enable increased wettability of the hydrophobic substrate, with polysaccharides outperforming proteins due to

the former's more marked polar nature. Among polysaccharides, the best performance in terms of decreased water contact angle was observed for molecules with amorphous organization, such as pullulan. The increased surface energy ensuing from the biocoating's deposition can be advantageously exploited for a number of packaging operations, such as the deposition of adhesives and inks or the generation of anti-fog materials (Introzzi *et al.*, 2012b).

Another important advantage linked to hydrocolloid based coatings (especially polysaccharides) is that their deposition does not affect the optical properties of the final materials. Such coatings, generally having a thickness ranging from 500 nm to 2 μm , do not absorb visible light; hence, they do not impair the so-called "see-through" capability of the final package, which is very important from an aesthetic point of view especially for freshly cut and minimally processed foods. Additionally, some polysaccharides can increase the optical properties of the plastic substrate (Introzzi *et al.*, 2012b; Cozzolino *et al.*, 2016a; Unalan *et al.*, 2017). Pullulan, for example, has been shown to increase the clarity of PET films due to its anti-reflection behavior, which in turn can be explained considering that the refractive index of pullulan is between those of air and PET (Unalan *et al.*, 2017).

Another use of biopolymer coatings lies in their capability to react to external stimuli such as temperature, pH, ionic strength, and especially moisture content. This capability has been proposed as a strategy to trigger the release of active compounds embedded in the main biopolymer phase into the food, possibly in a controlled manner over time (Barbiroli *et al.*, 2016). According to this principle, antimicrobial coatings based on hydrocolloids have been proposed as an alternative to the most common practice of adding the antimicrobial substance directly into the food matrix and can thus result in an active packaging material (Mascheroni *et al.*, 2011; Kurek *et al.*, 2013).

Hydrocolloids and Nanotechnology

The current use of hydrocolloids in the nanotechnology field relies on the capability of researchers to extract nanoparticles that may profitably be used as nano sized building blocks (NBBs) to produce high performance systems, e.g., new packaging and encapsulation materials. According to the most recent works on the use and application of organic nanofillers, the discussion in this section will center on four types of nanoparticles: cellulose in its manifold derivatives, starch nanocrystals, chitin whiskers, and amyloid fibers.

Cellulose-based fillers. Three main sets of cellulose nanoparticles can be obtained from the parental, macro-sized cellulose using proper methods. Microfibrillated cellulose (MFC) (Fig. 2a), also called nanofibrillated cellulose, cellulose nanofiber, and cellulose nanofibril, is obtained from both wood fibers and plant fibers by mechanical treatments, such as high-pressure homogenization, although chemical, physical, and enzymatic pre-treatments are increasingly used to decrease the very high energy consumption associated with the homogenization process. MFC fibrils have a high aspect ratio (diameter: 5-60 nm; length: from 100 nm up to several microns) and are characterized by both amorphous and crystalline regions (Moon *et al.*, 2011).

Cellulose nanocrystals (CNCs), interchangeably known as nanocrystalline cellulose, cellulose whiskers, cellulose nanowhiskers, and cellulose microcrystals, are mostly obtained by acid hydrolysis of native cellulose, although alternative methods (e.g., enzymatic hydrolysis) have been proposed recently (Rovera *et al.*, 2018). These processes allow removing the amorphous domains, thus yielding a totally crystalline substance in the form of rods (Fig. 2b). It follows that, unlike MFC, CNCs do not possess flexibility.

Bacterial cellulose (BC) (Fig. 2c), synonyms with bacterial nanocellulose, microbial cellulose, or biocellulose, is naturally crystalline, free from pectin, lignin, and hemicelluloses found in plant cellulose. The BC shows different fibril shapes (e.g. may vary from

rectangular to square and more or less cylindrical) with an aspect ratio usually larger than 50 depending on microbial species and nutrient media used in fermentation (Moon *et al.*, 2011). The interest in such a “green” filler lies in the possibility of exploiting the biotechnology approach to fine-tune shape, structure, and properties of the fibrils during biosynthesis to manipulate the final properties of the nanocomposite materials.

Cellulose nanoparticles in the food sector have been successfully used as a fat replacer, rheology modifier, as a support for immobilizing probiotics and enzymes, as emulsion stabilization, as reinforcement in food packaging materials, and as a building block for artificial meat (Khan *et al.*, 2018; Azeredo *et al.*, 2019).

Starch-based fillers. The interest in starch nanocrystals (SNCs) (Fig. 2d) hails from the material’s low cost, abundance, biocompatibility, biodegradability, and nontoxicity (La Corre *et al.*, 2010). Starch nanoparticles can be prepared according to three different routes, acid or enzymatic hydrolysis, regeneration, and mechanical treatment. These approaches allow obtaining starch nanoparticles with different properties, crystallinity, and shapes (La Corre *et al.*, 2010). For example, starch nanocrystals prepared by hydrolysis of native starch granules are platelet-shaped, 6–8 nm thick, 40–60 nm long, and 15–30 nm wide (Putaux *et al.*, 2003). As a consequence, the reinforcing capability of starch nanocrystals may be limited compared to cellulose nanocrystals, due to an inferior aspect ratio. Another limitation of starch nanocrystals is the duration of the hydrolysis process, which is much longer compared to cellulose, though faster procedures have recently been proposed (Dai *et al.*, 2019). However, all these drawbacks may be overcome by coupling starch nanocrystals with other natural fillers, e.g. cellulose nanocrystals (Silva *et al.*, 2019). Other strategies to enhance the properties of starch nanocrystals include the functionalization of the surface of starch nanocrystals in order to impart new functional properties (Hao *et al.*, 2019). Although most applications have been envisaged for the food packaging sector, recent studies have outlined

the potential use of starch nanocrystals for the manufacturing of nanocarriers for targeted delivery of nutraceuticals (Rostamabadi *et al.*, 2019) and as a fat replacer in reduced fat O/W emulsions (Javidi *et al.*, 2019).

Chitin-based fillers. Chitin, the second most abundant biopolymer in nature, is found in the exoskeleton of crustaceans, such as crab and shrimp shells as a byproduct of the seafood industry, cuticles of insects, and cell walls of fungi (Harish Preshanth and Tharanathan, 2007). Chitin is well-recognized as a biocompatible material because of its low antigenicity, low toxicity, and biodegradability (Dutta *et al.*, 2004). Chitin whiskers (Fig. 2e) of slender parallelepiped rods can be easily obtained using vigorous stirring in boiling HCl (Sriupayo *et al.* 2005). Depending on the origin, chitin whiskers range between 100 nm and 800 nm in length and from 5 to 70 nm in width (Tran *et al.*, 2019). Chitin whiskers have attracted much attention due to their unique cationic nature, which paves the way to synergistic associations with counter-charged nano-fillers (e.g. cellulose) (Irvin *et al.*, 2019). Chitin whiskers have been used to reinforce many polymeric matrices, including hydrocolloids such as chitosan (Sun *et al.*, 2018), alginate (Watthanaphanit *et al.*, 2008), and cellulose (Huang *et al.*, 2013). More recently, the use of chitin whiskers has also been proposed as a modulating agent of gelatinization and retrogradation of maize and potato starches (Ji *et al.*, 2017).

Amyloid-based fillers. Amyloid fibrils (Fig. 2f) have gained recent interest as a potential nanofiller in the design of renewable composite materials. New, exciting features of amyloid fibrils have been disclosed in the last years. Among others, unique physical aspects relying on the self-assembly properties of the fibrils have been reported Lara *et al.* (2011). Amyloid fibrils can be formed from many proteins via self-assembly (Ecroyd *et al.*, 2013), leading to insoluble fibers that are resistant to degradation. Amyloid fibrils are renewable, inexpensive, and can be potentially synthesized in industrial quantities from crude protein

sources. Amyloid fibrils are comprised of proteins with a highly ordered β -sheet structure (Serpell and Smith, 2000), a packing arrangement that provides both strength and thermochemical stability. Thus, they have been successfully used as a reinforcing agent of polymeric materials. Byrne *et al.* (2011) incorporated amyloid fibers generated from hen egg white lysozyme in an L-poly(lactic acid) (PLLA) matrix. In another study, researchers developed a method to fabricate films comprising amyloid fibrils formed from bovine insulin in a PVOH matrix (Rao *et al.*, 2012). Finally, researchers produced graphene–amyloid fibrils composites as a new class of biodegradable composite materials with adaptable properties (Li *et al.*, 2012). In this work, the developers used globular milk protein β -lactoglobulin as a source of amyloid fibers. More recently, amyloid fibrils were used as a stabilizing agent of Pickering emulsions (Wei *et al.*, 2019).

Hydrocolloids as Encapsulation Agents

The encapsulation is an increasingly popular and well developed technique in the food industry. The main principle of this technique is based on coating or entrapping the sensitive compounds within a small capsule (Jia *et al.*, 2016). The coated/entrapped compound is called core or active material, while the coating/entrapping material is called encapsulant, shell, wall, material, or carrier. The first step of encapsulation is the formation of emulsion/suspension with core and encapsulant materials. The second step is drying or cooling of the emulsion/suspension depending on applied encapsulation methods (e.g., physical methods: spray-drying, spray chilling/cooling, extrusion, fluidized bed coating; chemical methods: coacervation, co-crystallization, molecular inclusion, interfacial polymerization, etc.) (Madene *et al.*, 2006).

Different food hydrocolloids (proteins such as gelatin, caseinate, whey protein, soy protein, etc., and polysaccharides such as starch, maltodextrin, gum arabic, etc.) are used extensively in the encapsulation of colorants, flavor compounds, antimicrobials, antioxidants,

and bioactive compounds to improve their solubility, stability, bioactive properties, and bioavailability. The molecular (high MW and chain flexibility), rheological and surface active properties of proteins, as well as their ability to self-associate and to interact with different types of substances (Kim *et al.*, 1996) make them one of the most preferred encapsulant materials. Polysaccharides are also extensively used for encapsulation due to their good solubility, low viscosities at high solids contents, low cost, diversity, and widespread use in foods (Madene *et al.*, 2006).

The developments in the field suggest that the encapsulation of bioactive phenolics will continue to dominate the research studies related to encapsulation. Moreover, the use of probiotics as core material will also increasingly continue since microencapsulated probiotics show significantly higher gut colonization than uncoated probiotics (Corrêa-Filho *et al.*, 2019; Del Piano *et al.*, 2011). Currently, microcapsules based on alginates, blends of alginates with milk or whey proteins, and chitosan-coated alginates (applied by layer-by-layer strategy) are used successfully to improve viability and colonization of probiotics at gastric conditions (Shori, 2017). However, further studies are also needed to increase the viability of probiotics at food processing conditions. Furthermore, in recent years, the use of encapsulated bacteriophages has been researched to get rid of the negative aspects of antibiotics used in food-animal production. Thus, investigation of the most effective encapsulation materials and methods for preservation of bacteriophage activity against adverse conditions (e.g. during feed preparation, at gastrointestinal conditions of animal, and during food processing) will also be a significant issue of future studies (Choińska-Pulit *et al.*, 2015).

Hydrocolloids and Human Health

The dietary hydrocolloids influence human health in two major ways: 1) regulation of physical effects such as gastric emptying time, intestinal nutrient passage rate, nutrient absorption, and digestion, and 2) inducing molecular and cellular effects.

Hydrocolloids in the food matrix might decrease carbohydrate, lipid, and protein digestion enzyme activities by binding active site of enzymes or blocking enzyme and substrate interactions. For example, hydrocolloids such as chitosan and alginate retard the digestion of emulsified lipids by different mechanisms. It is thought that chitosan limits access of lipase to lipid droplets by its ability to promote lipid droplet aggregation through bridging flocculation while alginate does the same function by sequestering calcium ions and promoting depletion flocculation of emulsified lipid droplets (Qin *et al.*, 2016). Distraction between enzymes and substrates also causes incomplete digestion of macronutrients in the small intestine, and those nutrients are not substrates for intestinal transporter proteins (Merga *et al.*, 2014). They also increase nutrient transit time and the viscosity of the lumen, resulting in a low level of the nutrient absorption through enterocyte cells of the intestine. Moreover, hydrocolloids dependent high viscosity in the stomach leads to prolonged satiety, which is vital to control energy intake and weight management.

The interactions of hydrocolloids should also be considered during their food applications since some hydrocolloids could interact with phytochemicals, vitamins or minerals to decrease their bioavailability in the small intestine (Gao *et al.*, 2017). Humans do not have any digestion mechanism for some dietary hydrocolloids (e.g., inulin, pectin and resistant starches); however, they can be metabolized in the colon (especially in cecum) by bacteria. These hydrocolloids called prebiotics show their effect on human health by increasing the number of good bacteria and the production of short chain fatty acids (SCFAs) including acetate, butyrate, and propionate. The physiological roles of the SCFAs have been

recently elucidated in *in vivo* studies. SCFAs influence immunity (D'Souza *et al.*, 2017) and cancer (Wang *et al.*, 2019) via cytokine production and controlling cell growth rate, respectively. A high-fat diet with high butyrate showed increased energy expenditure and reduces obesity risk in mice (Lu *et al.*, 2016). Furthermore, propionate esters from inulin induced postprandial GLP-1 and PYY peptides in human, resulting in the reduction of calorie intake (Chambers *et al.*, 2015). Pectin also has a similar effect on energy metabolism in *in vivo*. Pectin with high and low-fat diets lead to a decrease in the levels of leptin, insulin, and total cholesterol, and triglycerides (Adam *et al.*, 2015). The pectin in diets of rat also increased PYY level, indicating that fermentation of pectin promotes health benefit regardless of high or low-fat diets (Adam *et al.*, 2015). Toll-like receptor (TLR) family is essential for innate immunity signaling mechanisms, which involve in allergy, asthma, and inflammation of gastrointestinal tract, and cancer (Gay *et al.*, 2006, Akira and Takeda 2004). It has also been shown that pectin can bind to TLR2 protein and inhibits TLR2-TLR1 regulated proinflammatory response in *in vitro* via blocking the interaction between TLR2 and TLR1 (Sahasrabudhe *et al.*, 2018). Moreover, the sweet green paper derived pectic polysaccharides has an antineoplastic effect (for instance inhibition of a tumor) by controlling inflammation and angiogenesis in tumor-injected mice (Adami *et al.*, 2018). Another health promoting hydrocolloid is high-amylose maize resistance starch type 2 (HAM-RS2), which is involved in carbohydrate metabolism in obesity. Consumption of HAM-RS2 improves glucose homeostasis and lowers leptin levels in overweight humans (Maziarz *et al.*, 2017).

Hydrocolloids are also used as a functional delivery system into the human body and cells of organs. It has been shown that pectin coated iron particles are highly bioavailable compared to free iron in *in vivo* (Moslemi *et al.*, 2018). Lipid-emulsified alginate beads might be a straightforward approach to control weight management via reduction of food intake (Corstens *et al.*, 2019). Inulin can be utilized as a carrier for short interfering RNA (siRNA),

which is used to control gene regulation in the mammalian cells (Cavallaro *et al.*, 2017). Pectin/zein hydrogels have been used as a carrier for p40, *Lactobacillus rhamnosus* GG-derived protein, which plays a role in intestinal maturation and innate immunity (Shen *et al.*, 2018).

The current evidence suggests that subunits of polysaccharide source hydrocolloids have direct effects on molecular and genetic responses on the cells. The hydrocolloids can be hydrolyzed by enzymes, chemicals or physical methods. The oligosaccharides from a hydrolyzed form of pectin subunits (POS) have significant roles in health including colon cancer, diabetes, hypercholesterolemia, and inflammation (Tan *et al.*, 2018). POS have direct interactions on molecular mechanisms of the cells. Thus, the interaction between POS and the cellular mechanism will open the idea to provide therapeutic approaches in clinical practice. Moreover, degraded units of hydrocolloids and their possible cellular impact in human physiology should be evaluated to determine molecular mechanisms that might be controlled by hydrocolloids.

Protein isolates are another group of hydrocolloids, and they might have a health impact on human. The health benefits of proteins are related to the antioxidant activity of peptides generated after their digestion. The peptides owe their antioxidant activity to their constituent amino acids such as aromatic, sulfur-containing and basic amino acids capable of donating protons to free radicals (Arcan and Yemenicioğlu, 2010). It has been shown that protein hydrolysates are involved in GLP-1 and CCK hormones, indicating that bioactive peptides might be used to control both food intake and body weight management (Geraedts *et al.*, 2011). Furthermore, whey peptides rich supplementation might improve cognitive function in adults, suggesting that whey peptides might be beneficial for fatigue in adult subjects (Kita *et al.*, 2018). It has been suggested that milk protein supplementation in healthy man leads to increase bone formation and decrease bone resorption in term of urinary

markers (Toba *et al.*, 2001). Digested germinated soybean peptides showed anticancerogenic effect on human colorectal cells, and in the same study, the peptides also decrease proinflammatory markers in mouse macrophage cells (Gonzalez-Montoya *et al.*, 2018).

Another health benefit of hydrocolloids is observed when they are used to formulate texture modified foods (TM foods) that refer to food with soft textures and/or reduced particle size as well as thickened liquids (drinks) that designed for elderly people with eating dysfunctions (Aguilera and Park, 2016). The hydrocolloids are employed to obtain soft microgel particles and fibers suitable for formulation of TM foods of elderly people suffering from masticatory/swallowing dysfunctions (Aguilera and Park, 2016). Moreover, hydrocolloids (e.g., starches and xanthan gum) could be used to slow down the flow of drinks designed as TM food, and to prevent their aspiration through the airway during consumption (Aguilera and Park, 2016; Martínez *et al.*, 2019).

All these discussions clearly showed that extensive future studies are needed to clarify hydrocolloid-health interactions and enlighten a specific range of hydrocolloids' impacts on human health. The interactions of different types of hydrocolloids and their hydrolysis products with probiotics and the effects of these interactions on SCFAs produced should be investigated to determine the specific health benefit of polysaccharide source hydrocolloids. It has been indicated that the cellular effect of SCFAs is mainly type and dose-dependent. Thus, it should be considered that which type of dietary hydrocolloids are used for health purposes during food formulation. Bacteria species, which can be affected by dietary hydrocolloids, should also be considered since health effects depend highly on type and amount of SCFAs they produce. Recent studies show that hydrocolloids and their hydrolysates have direct and specific effects on molecular mechanisms of human physiology. Thus, it is essential to combine molecular approaches with hydrocolloids research in cell culture, animal and human studies. Furthermore, possible adverse effects of hydrocolloids

should be taken into consideration when they are used in terms of health. More molecular dependent mechanistic studies will open new areas for the use of hydrocolloids as functional additives, ingredients, and medical food in the new future.

Conclusions and future studies

This review discussed the dynamic developments and future trends in the fields of food hydrocolloid research and applications. Players and stakeholders of the sector should continuously monitor the new trends in the field, especially concerning aspects related to health, religion and environment, demands of emerging fields, economic and technological issues, and consumption habits of consumers. Particular efforts are also needed to improve molecular and biotechnological methods that could be employed in the next production and tailoring of hydrocolloids. Moreover, current developments clearly showed that exploiting interactions of hydrocolloids with food components, combinational use of hydrocolloids to discover their potential synergies, and nanotechnology routes are primary tools to meet future consumers' and food sector's demand for sophisticated technological functions. It is also obvious that the increased use of natural hydrocolloids in food packaging might be an effective solution to control environmental problems caused by plastics world-wide. Finally, further studies are needed to investigate positive and negative effects of natural and modified hydrocolloids on human health and regulate their food applications accordingly.

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Data availability

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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Table 1. Major interactions of hydrocolloids with food components

Interactions	Mechanism/Effects of interaction	References
Protein-Water	Protein–water interactions by hydrogen bonding.	Sikarski <i>et al.</i> (2007)
Protein-Protein	Covalent/noncovalent intermolecular binding/change hydration, solubility, viscosity, film formation, gelling, and surface activity.	Gao <i>et al.</i> (2017)
Protein-Polysaccharide	Complexes formed by ionic interactions and H-bonding/modifies different functional properties.	Gao <i>et al.</i> (2017)
Protein-Lipid	Non-covalent lipid protein complexes form by hydrophobic interactions/affect surface activity.	Sikarski <i>et al.</i> (2007)
Protein-Mineral	Binding of minerals by specific groups, and ionic interactions/surrounding “ion atmosphere” affects solubility, rheological and gelling properties of protein.	Cao <i>et al.</i> (2016)
Protein-Tannin	Hydrophobic interactions/modify protein functionality, solubility and nutritive value.	Jauregi <i>et al.</i> (2016)
Protein-Carbonyl (or lipid oxidation products)	Maillard and Strecker degradation/decreases nutritive value of proteins, modifies texture, color, flavor of food.	Sikarski <i>et al.</i> (2007)
Polysaccharide-Water	A very viscous and pseudoplastic solution forms even at low concentrations.	Sikarski <i>et al.</i> (2007)
Polysaccharide-Polysaccharide	H-bonding/affects viscosity, setting rate and rheological properties of gels.	Sikarski <i>et al.</i> (2007)
Polysaccharide-Lipid	Hydrophobic effects.	Sikarski <i>et al.</i> (2007)
Polysaccharide-Mineral	Egg-box model binding/surrounding “ion atmosphere” affects solubility, rheological and gelling properties.	Cao <i>et al.</i> (2016)

Table 2. Effects of interactions between some hydrocolloids and phenolic compounds

Hydrocolloids	Polyphenols	Effects of interaction and related reference
Alginate, Pectin, Locust bean gum	Anthocyanins	Hydrocolloids prevent water attack and condensation reactions that reduce color stability of anthocyanins (Hubbermann <i>et al.</i> , 2006).
Casein	Curcumin	Casein increases water solubility, antioxidant activity and cell proliferation of curcumin (Pan <i>et al.</i> , 2013).
Zein	Curcumin	Zein increases mucoadhesion and stability of curcumin at gastrointestinal conditions (Patel <i>et al.</i> , 2010).
Zein	Catechin, gallic acid	Catechin and gallic acid increase flexibility of classically brittle zein films and coatings (Arcan and Yemenicioğlu, 2011)
Methylcellulose (MC)	Tannic acid (TA)	TA causes loss of thermo-reversible gelling of MC, but improves its emulsifying and foam-stabilizing properties (Patel <i>et al.</i> , 2013)
Whey protein	Green tea polyphenols	Polyphenols improve the firmness and adhesiveness of whey protein gels at pH 6.0 (Von Staszewski <i>et al.</i> , 2011).
Gelatin	TA	TA increases mechanical stability and rigidity of gelatin gels at pH 8.0 (Zhang <i>et al.</i> , 2010)
Ovalbumin	Tea polyphenol (TP)	Ovalbumin interacted with TP digested more rapidly by pepsin, but its digestibility by pancreatin is inhibited (Shen <i>et al.</i> , 2014)

Table 3. Selected commercially important food applications of major hydrocolloids

Hydrocolloid	Selected applications	Major benefit	References
Gelatin	Low-fat and reduced calorie products	Fat replacer (Gelation, texturization, water binding)	McClements (2015)
	Confectionary	Gelation, foaming, texturization	Mariod and Fadul (2013)
	Dairy products	Stabilization, texturization, emulsification	
	Meat products	Gelation, water binding, adhesion, emulsification	
Egg proteins	Bakery products	Adhesion and binding of ingredients, gelation, water binding, foaming, texturization	Damodaran and Paraf (1997)
Whey proteins	Nutritional beverages, bars and yogurts	Nutritive value, direct physiological effects when consumed in conjunction with human performance activities	Kelly (2018)
	Reduced fat cheeses	Fat replacer	
Caseinates	Processed cheese	Emulsification, texturization	
	Meat, fish, poultry products	Emulsion stabilization	
Milk protein concentrates	Meat products	Emulsification	Patel and Patel (2014)
	Soaps, sauces, yogurt, beverages	Thickening, emulsification, heat stability	
	Pediatric, geriatric, medical, sports nutrition products	Nutritive value, source of bioavailable calcium	
Pectin	Jams and jellies,	Gelation	Ciriminna <i>et al.</i> (2016)
	Beverages, yogurt, yogurt and soy drink, dressings	Thickening, suspending, stabilization, texturizing	
Alginate	Sauces of canned food	Thickening after sterilization improves heat transfer	Featherstone (2015)
	Beverages, dressings, sauces	Thickening	
Starches	Soaps and sauces	Thickening	Saha and Bhattacharya (2010)
Resistant starches	Bakery products	Provide health benefits, increase satiation, reduce energy	Fuentes-Zaragoza <i>et al.</i> , (2010)

Table 4. Different examples of biopolymer coatings based on hydrocolloids deposited on food packaging materials.

Hydrocolloid	Substrate ^a	Properties gained	Reference
WPI	PP	Oxygen barrier	Hong and Krochta (2003); Hong and Krochta (2004)
WPI	PB	Grease barrier, color	Lin and Krochta (2003)
WPI	PP, PVC	Optical, surface	Hong <i>et al.</i> (2004)
WPI, WPC	PP, PE	Oxygen barrier	Hong and Krochta (2006)
MCC, HMPC, chitosan, κ -carrageenan, dextrin	PP	Optical, tensile, antimicrobial	Hong <i>et al.</i> (2005)
Gelatin	PET	Antimicrobial	Barbiroli <i>et al.</i> (2016)
Gelatin	PP, PE, PET	Oxygen and water vapor barrier, optical, friction,	Farris <i>et al.</i> (2009a)
Gelatin	PP	Sealing	Farris <i>et al.</i> (2009c)
Gelatin	PP	Sealing	Farris <i>et al.</i> (2010)
Wheat gluten	Paper	Antimicrobial	Mascheroni <i>et al.</i> (2011)
Gelatin, chitosan, pectin, pullulan	PET	Surface	Farris <i>et al.</i> (2011b)
Chitosan	PE	Oxygen, carbon dioxide, and water vapor barrier	Kurek <i>et al.</i> (2012a)
Chitosan	PLA	Oxygen barrier, optical	Svagan <i>et al.</i> (2012)
Chitosan	PE	Adhesion, wettability, antimicrobial	Kurek <i>et al.</i> (2013)
Chitosan	PE	Thermal properties	Kurek <i>et al.</i> (2012b)
Chitosan	PE	Oxygen, water vapor, grease, and UV-light transmission	Vartiainen <i>et al.</i> (2010)
Pullulan	PET	Antifogging	Introzzi <i>et al.</i> (2012a)
Pullulan	PET	Oxygen barrier	Farris <i>et al.</i> (2012)
Pullulan	PET	Oxygen barrier	Fuentes-Alventosa <i>et al.</i> (2013); Introzzi <i>et al.</i> (2012b); Unalan <i>et al.</i> (2016); Unalan <i>et al.</i> (2017)
Pullulan	PET	Nanomechanical	Rovera <i>et al.</i> (2018a)
Pullulan	PP	Oxygen barrier, mechanical,	Cozzolino <i>et al.</i> (2016a);

		surface	Cozzolino <i>et al.</i> (2016b)
CMC and chitosan	PB	Oil and water vapor barrier, mechanical	Basu <i>et al.</i> (2017)
HPMC	PLA	Optical, antifogging	Zhang <i>et al.</i> (2018)

^aPolypropylene (PP), Polyethylene terephthalate (PET), Poly(lactic acid):PLA; Polyethylene (PE); polyvinyl chloride (PVC); Paperboard (PB)

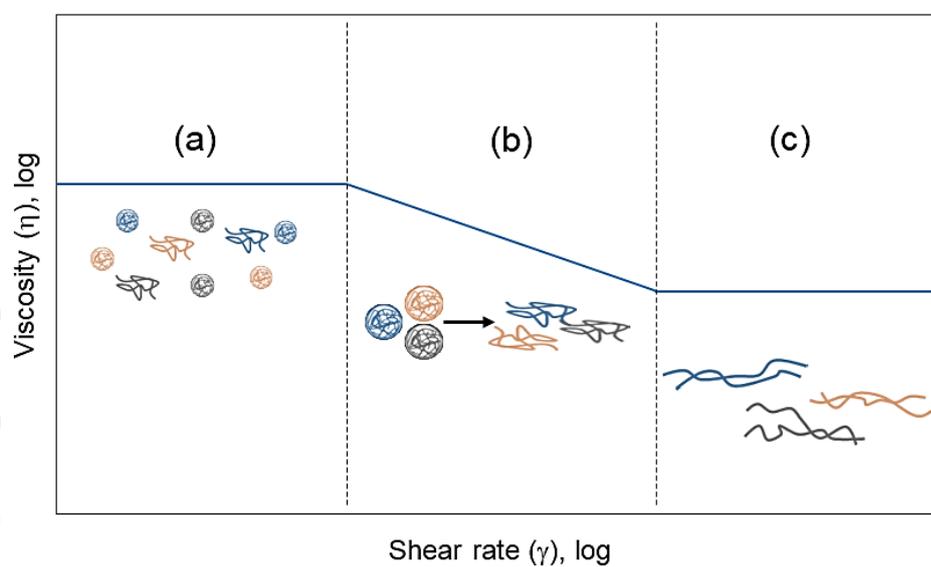


Figure 1. Schematic representation of the viscosity-shear rate behavior of hydrocolloid polymer solutions above C^* (adapted from Khatibi *et al.*, 2016).

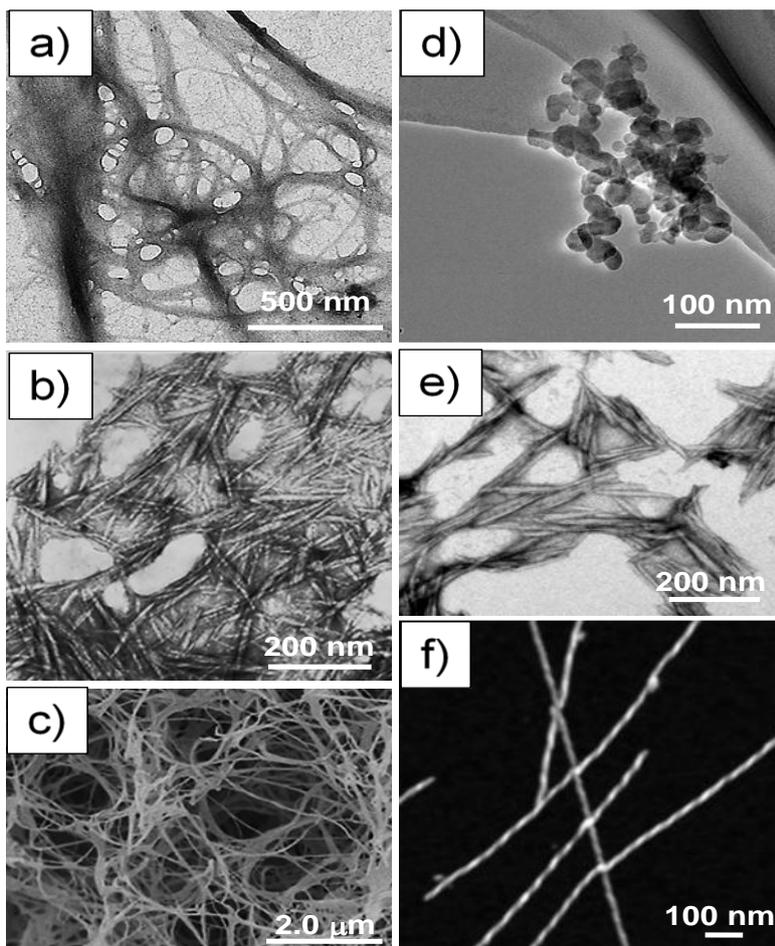


Figure 2. TEM images of a) MFC and b) CNCs; SEM micrographs of c) BC; d) SNCs (reproduced with permission from Elsevier Ltd [Wang *et al.*, 2010]); e) chitin nanocrystals (reproduced with permission from Elsevier Ltd [Wang *et al.*, 2012]); f) AFM image of amyloid fibrils with twisted ribbon morphology (reproduced with permission from Elsevier Ltd [Adamcik and Mezzenga, 2012]).