



Hydrocolloid and water soluble polymers used in the food industry and their functional properties: a review

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Abstract

Hydrocolloids in foods play a vital role in developing food systems with enhanced rheology, quality, organoleptic properties and nutritional value in food industry. Hydrocolloids possess the ability to modify viscosity and texture of a food system. Modification of viscosity and texture in a food will directly affect for the sensory attributes of a food product. Enhancement of these attributes leads to increased consumer acceptance towards the developed food product. Hydrocolloids of natural, semi-synthetic and synthetic origin could be used in the food industry. However, natural hydrocolloids are most preferred due to their inherent benefits. Hydrocolloids have the possibility to function as, thickeners, gelling agents, emulsifiers and stabilizers while they also have applications in development of edible films and edible coating formulations. Beside these inherent functional properties, hydrocolloids have become attractive due to their dietary fibre aspect which provide a wide array of health benefits to the consumer. Hence, hydrocolloids act as health promoters by reducing the risk of cardiovascular diseases, reducing the risk of obesity, regulating glycemic response and maintaining colonic health. This review provides a discussion on food hydrocolloids, their basic functionality, properties and applications in food industry.

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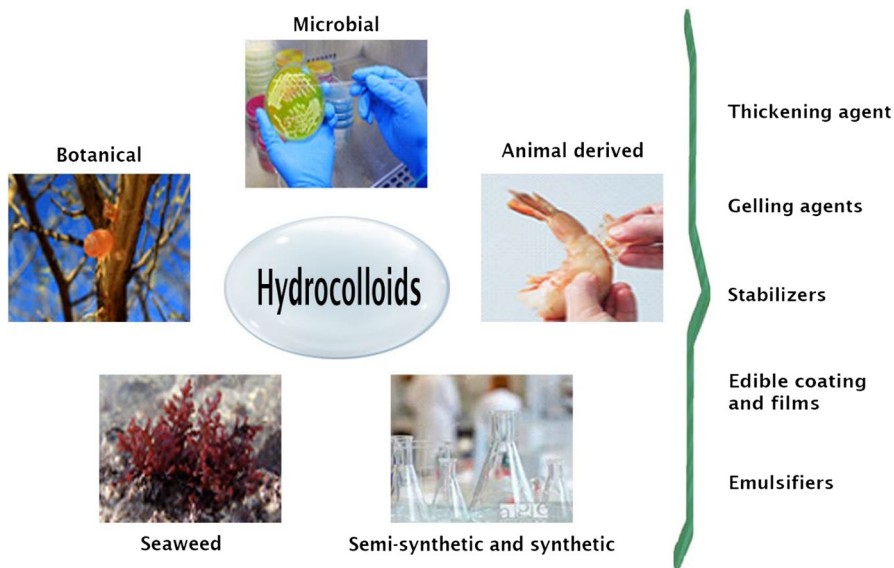
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Graphical abstract



Keywords Polymers · Hydrocolloids · Rheology · Functions · Properties · Food applications

Introduction

At present, research in the field of food science are focusing on fabrication of different colloidal systems enhancing rheology, quality, organoleptic properties and nutritional value [1]. Thus, hydrocolloids play a vital role in achieving this target. Due to these recent trends, hydrocolloid production and sales is increasing globally. According to data stated in studies, the hydrocolloid market valued 5.70 billion in 2015 and it is estimated to reach 7.56 billion by 2020 [2]. These data denote the industrial importance achieved by hydrocolloids in recent years.

Hydrocolloids can be defined as heterogeneous group of long chain polymers which form viscous dispersions and/or gels when dispersed in water. Hydrocolloids can be either polysaccharides or proteins [3]. Gelling, thickening and stabilising functions of hydrocolloids are used in different industrial sectors, especially in food industry. These polymers are comprised of a large number of hydroxyl groups. These hydroxyl groups increase their affinity for binding with water molecules making them hydrophilic. Further, these polymers exhibits the properties of a colloid by producing a dispersion, which is intermediate between a true solution and a suspension. Thus, considering these two properties, these polymers are named as hydrophilic colloids' or 'hydrocolloids' [3].

Hydrocolloids are commonly used in food products such as, yoghurt, ice creams, sauces, dressings and mayonnaise. They provide functions such as thickeners, gelling agents, foaming agents, acting as edible coatings, emulsifiers and stabilizers in food systems [4]. Hydrocolloids have the ability to modify the flow behaviour which is termed as viscosity and mechanical solid property which is termed texture of a food. Modification of viscosity and texture in a food will directly affect for the organoleptic properties which determine the consumer acceptance of a food. Thus, hydrocolloids are an important group of food additives used in the food industry [3].

Beside these inherent functional properties, hydrocolloids have become attractive due to its dietary fibre aspect which provide a wide array of health benefits to the consumer. Most food hydrocolloids fall in to the category of dietary fibre. Thus, there are instances where hydrocolloids are used to increase the fibre content of food products [4]. Fibre is an important ingredient in a healthy diet. The recommended average daily intake value of dietary fibre in the USA and UK is 25–30 g and more than 18 g, respectively [5, 6]. Intake of dietary fibre would provide health benefits such as prevention of cardiovascular diseases, proper weight management, postprandial blood glucose level, regulate glycemic response and maintenance of colonic health [4, 6, 7].

Based on the existing literature available on food hydrocolloids, it will be interesting to review about these hydrocolloids and their functional properties when being incorporated into several food products. Thus, this review aims at highlighting the main intrinsic functions of food hydrocolloids used in food industry.

Classification of hydrocolloids

Hydrocolloids are categorized as natural, semi-synthetic and synthetic considering their origin. Natural hydrocolloids which are the most preferred hydrocolloid group in food industry are introduced as hydrophilic polymers that are originated from natural sources such as microorganisms, plants, animals, and seaweeds. Semi-synthetic hydrocolloids are introduced as hydrocolloids which are obtained by modifying the natural sources while synthetic hydrocolloids are the hydrocolloids which are completely synthesized from petroleum-derived base materials by chemical processes in order to produce a product with structure similar to the structure of naturally derived polysaccharides [1]. Classification of hydrocolloids is shown in Fig. 1.

Natural hydrocolloids

Natural hydrocolloids are widely used in the food industry. The advantages of using natural hydrocolloids over synthetic hydrocolloids include biocompatibility, non-toxic nature, easiness of handling, capability of modifying physically or chemically, eco-friendliness, cost-effectiveness, and more public acceptance since the polymers are extracted from natural renewable sources [1]. However, disadvantages of natural hydrocolloids over synthetic and semi-synthetic hydrocolloids are that its requirement to be incorporated in high quantities to be effective as emulsifiers and the

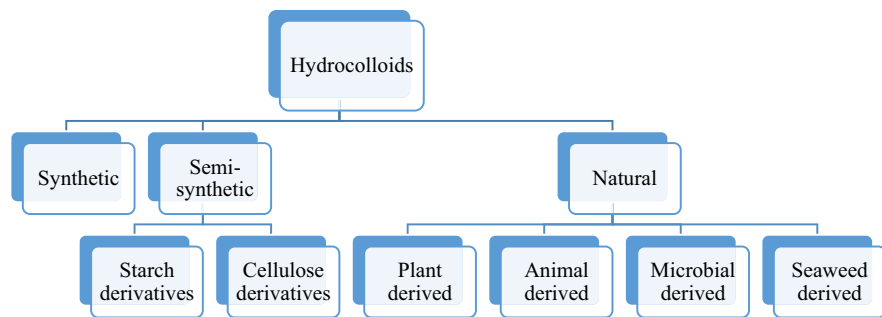


Fig. 1 Classification of hydrocolloids (Source [1])

susceptibility to microbial degradation [8]. Main sources of natural hydrocolloids are tabulated in Table 1.

Plant-derived cellulose is a commonly used hydrocolloid which could also be modified in to variety of semi-synthetic hydrocolloids. Generally, cellulose is obtained from wood. However, non-wood sources such as cotton fibre, pea hull fibre, ramie fibre, banana fibre, sisal fibre, kenaf pulp, and flax fibre could also be used. Exceptionally to those sources bacteria, algae, and marine tunicates could also be used in cellulose production [11]. Starches are also an important natural food hydrocolloid. As starches, corn, rice, potato, wheat, and tapioca starch are popular in food industry. Functional properties of native starches in food systems differ depending on their granule size and amylose to amylopectin ratios [11]. Pectin is another hydrocolloid which is of high interest. Pectin is widely extracted from citrus peels and apple pomace. However, due to high demand for pectin in food industry, alternative sources such as sunflower heads and sugar beet pulp are also utilized in extracting pectins. Major industrially utilized pectin forms are high-methyl ester pectin (HMP, and pectins obtained by HMP modification such as low-methyl ester pectin (LMP) and amidated low-methyl ester pectin [11]. Gums derived from different plants are also used as hydrocolloids in food

Table 1 Sources of natural hydrocolloids (Source [9–12])

Botanical	Plant polysaccharides—Cellulose, starch, pectin
	Tree gum exudates—gum Arabic, gum karaya, gum ghatti, gum tragacanth, cashew gum
	Seeds—guar gum, locust bean gum, Basil seed gum, tara gum, tamarind gum, balangu seed gum, wild sage seed gum, cress seed gum
	Plant proteins—Soy proteins, pea, hemp and potato protein isolates
	Tubers—konjac mannan
Animal	Gelatin, whey protein, chitosan, caseinate, egg white protein
Seaweed derived	Red seaweeds—agar, carrageenan
	Brown seaweeds—alginate
Microbial	Pullan, xanthan gum, gellan gum, cellulose, dextran, curdlan

industry. Guar gum of seeds of the tree *Cyamopsis tetragonoloba*, locust bean gum of seeds of the carob tree *Ceratonia siliqua*, karaya gum of *Sterculia urens tree*, gum tragacanth from stems and branches of Asiatic species of *Astragalus*, basil seed gum of *Ocimum basilicum*, balangu seed gum of *Lallemantia royleana*, tara gum of the seeds of *Caesalpinia spinosa*, wild sage seed gum of *Salvia macrosiphon*, cress seed gum of *Lepidium sativum* and gum Arabic as an exudate of mature trees of *Acacia Senegal* and *Acacia seyal* are also used in the food industry [10, 11, 13].

Animal-derived hydrocolloids have mostly originate from skins and bones of animals such as swine and cattle. Examples for animal derived hydrocolloids are given in Table 1. Gelatin is the most widely used animal-derived hydrocolloid which accounts for around 99% of the overall market of animal hydrocolloids [1]. Gelatin is a non-immunogenic protein-based biodegradable hydrocolloid which is comprised of repeating sequences of glycine-proline-hydroxyproline amino acids over the polymer chain to form a triple helical structure. It is mostly extracted from animal connective tissue (collagen) found in skins or bones of different animal species such as cows, pigs, fish and poultry [1, 14]. Whey protein or serum protein is another possible hydrocolloid. It is the main by-product of cheese manufacturing which possess a high nutritional value and biocompatibility. There is a possibility of using whey as a hydrocolloid in food products due to its large range of applicability to forms gels, emulsion and gelled emulsion [1]. Chitosan is another popular hydrocolloid which is used in the food industry. Chitosan is obtained by deacetylation of chitin [15]. Chitosan can be obtained from exoskeleton of crustaceans, invertebrates and fungi. It is composed of random molecules of β -(1–4)-linked D-glucosamine and N-acetyl-D-glucosamine in the linear polysaccharide chain [16].

Seaweed-derived hydrocolloids have also gained a popularity in the food industry. Agar and carrageenans which are extracted from red seaweeds (Rhodophyceae) and alginate which is extracted from brown seaweeds (Phaeophyceae) are the main seaweed-derived hydrocolloids utilised in the food industry. Agars are most commonly extracted from red seaweeds *Gelidium* and *Gracilaria* [17]. Carrageenan can be extracted from red algae varieties such as *Chondrus*, *Gigartina*, *Euचेuma* and *Hypnea* [18]. Alginate can be extracted from brown algae varieties such as *Macrocystis*, *Laminaria*, *Ascophyllum*, *Ecklonia*, *Eisenia*, *Nereocystis* and *Sargassum* [19, 20]

Extracellular polysaccharides produced by microorganisms are accounted as microbial hydrocolloids. Major microbial food hydrocolloids include fungal polysaccharides such as pullulan from *Aureobasidium pullulans* and bacterial exopolysaccharides such as xanthan gum from *Xanthomonas campestris*, gellan from *Pseudomonas elodea*, and cellulose from *Komagataeibacter xylinus* and *Acetobacter xylinum* [11]. Among microbial hydrocolloids xanthan gum accounts for over 90% of the global food market for microbial hydrocolloids [1].

Semi-synthetic hydrocolloids

Semi-synthetic hydrocolloids are produced through chemically modifying the hydrocolloids obtained from natural sources. Semi-synthetic hydrocolloids are stronger emulsifiers, non-toxic and less likely to undergo microbial growth [8].

Cellulose derivatives and starch derivatives are promising hydrocolloids which are classified under semi-synthetic hydrocolloids. Cellulose derivatives can be made by etherification, esterification, crosslinking or graft copolymerization of cellulose. Etherification of cellulose yields cellulose derivatives such as hydroxypropyl methylcellulose (HPMC) and carboxyl methylcellulose (CMC). Esterification of cellulose results cellulose derivatives such as cellulose acetate and cellulose acetate phthalate [12]. Sodium salt of CMC is a major derivative used as a hydrocolloid in the food industry. Methylcellulose (MC) and hydroxyethyl cellulose (HEC) are some other chemically modified derivatives of cellulose. Other than that, nanofibrillated cellulose and microcrystalline cellulose (MCC) are also cellulose derivatives which could be obtained by physical modification of cellulose [11].

Acetylated starch (AS), phosphorylated starch (PS), and hydroxypropylated starch (HPS) are examples for starch derivatives which could be used as semi-synthetic hydrocolloids [8].

Synthetic hydrocolloids

Synthetic hydrocolloids are chemically produced hydrocolloids. These are basically derived from chemical combinations to give a product having a structure similar to the naturally derived hydrocolloids. Acrylate copolymers, carboxyvinyl polymers (Carbopol), polyethylene oxide polymers (Polyox) and polyvinylpyrrolidone (PVP) are examples of synthetic hydrocolloids. Synthetic hydrocolloids could be considered as the strongest emulsifiers. Another advantage is that they do not support microbial growth. The synthetic hydrocolloids are mainly limited to use as oil-in-water emulsifiers [8, 21]. However, there are few disadvantages which could limit the usage of synthetic hydrocolloids in food industry. Those disadvantages include high production cost, toxicity to the consumers, high environmental pollution during the synthesis process and poor biocompatibility compared to naturally derived sources [8].

Functional properties of hydrocolloids

Hydrocolloids have gained an attention in different sectors such as food, pharmaceutical, biotechnology, agricultural and chemical industries. Hydrocolloids have become attractive in food industry since they are capable of altering the rheology of food systems. Alteration of rheology could result in food systems with modified sensory properties with higher consumer acceptance. Thus, permitted hydrocolloids are used as significant food additives in food systems to perform specific purposes in different food systems [22]. Those specific purposes of hydrocolloids in food systems include acting as thickeners, gelling agents, emulsifiers, encapsulating agents, fat replacers, adhesives and coating agents in food systems.

Thickening properties

Hydrocolloids are commonly used as thickening agents in different food systems. Thickening is the property of hydrocolloids that involves nonspecific entanglement of conformationally disordered polymer chains with solvent. This phenomena occurs only above critical concentration known as overlap concentration (C^*) [1]. Below the overlap concentration, the polymer chains in the polymer dispersion act as random coils of disordered arrangement. Thus, these polymer dispersions behave as Newtonian fluids that does not exhibit thickening property. However, at concentrations above the overlap concentration, polymer chains contact with each other and are less mobile resulting thickening. When thickening is taking place, polymer dispersions exhibit a non-Newtonian behaviour [9]. Thickening effect of hydrocolloids is governed by the type of hydrocolloid used, concentration of the hydrocolloid used and the properties of the food system such as temperature and pH [3].

Generally, hydrocolloids which have the potential to give a higher viscosity at relatively low concentration are most preferred in food products. Intrinsic viscosity (η) is a parameter used to compare the viscosities of hydrocolloid dispersions. Intrinsic viscosity can be correlated with the molecular mass of the hydrocolloid (M) by Mark–Houwink relationship which is shown in the following equation [3, 7].

$$\eta = KM^\alpha \quad (1)$$

where M is the molecular weight and K and α are the parameters of Mark–Houwink equation.

Thus, according to the equation, higher the molecular weight of the polymer, greater the intrinsic viscosity produced by the hydrocolloid in an aqueous medium. Except for molecular weight, factors such as hydrodynamic size and presence of charged polymers may also have a significant effect on thickening efficiency. Linear molecules with the larger hydrodynamic size give much higher viscosity than highly branched and highly flexible polymers of the same molecular mass. On the other hand, when there are ionic functional groups present in the polymer chain of the hydrocolloid, it causes expansion of polymer chains due to intermolecular charge repulsions. This result solutions with higher viscosity than a solution with non-ionic polymers with a similar molecular mass. Thus, this shows that hydrocolloids with a high molecular mass and a linear structure with charged functional groups are more pronounced thickeners [11].

Gelling property

In the food industry, there are wide array of food products which are marketed as gels. They include jams, jelly, desserts, fruit jellies, certain confectionary products, salad dressings, marmalade, etc. Hydrocolloids which perform the function of gelling agents play a vital role in determining the texture and other sensory attributes of these food products. Generally, gel character and texture of gels formed by gelling agents vary widely. Polysaccharide hydrocolloids such as natural gums, starches,

pectins, agar–agar and certain proteins such as zein from corn are commonly used as gelling agents in food industry [23].

Gelation could be defined as a process of phase transformation of a high molecular aqueous dispersion which is termed as a sol to a colloidal dispersion or a gel. In this phenomena, formation of inter-molecular interactions between sol particles by association or crosslinking of polymer chains hinders the flow ability of the sol and forms a three dimensional stable structure which is resistant to external stresses [1]. Water molecules will be trapped within the structure making them immobilize. Gels can be further introduced as viscoelastic systems. These systems have a storage modulus (G') larger than the loss modulus (G'') [23]. The associated regions with two or more polymer chains during gelation are known as 'junction zones' [3]. There are 3 mechanisms proposed for gelation of hydrocolloids. Those mechanisms include ionotropic gelation, cold-set gelation and heat-set gelation [24]. Ionotropic gelation is the gelation which occurs through crosslinking of hydrocolloid chains with ions, typically a cation-mediated gelation process of negatively charged polysaccharide polymer chains. The absence of specific ions at appropriate concentrations weakens the gelation property of certain hydrocolloids such as alginate, carrageenan, and pectin [25].

Ionotropic gelation

Ionotropic gelation can be carried out by the two techniques known as diffusion setting and internal gelation. Diffusion setting involves the introduction of a hydrocolloid solution to an ionic solution. There, gelation occurs through diffusion of ions into the hydrocolloid solution. The main disadvantage of internal gelation is the inhomogeneous gelation of gel particles. Internal gelation has become successful in overcoming the main disadvantage of diffusion setting. Internal gelation involves incorporation of an inactive form of the ion that will cause crosslinking of the hydrocolloid, which is then activated by a change in another parameter such as pH after sufficient dispersion of the ion is complete [24].

Cold-set gelation

In cold-set gelation, the solution is needed to be made by dissolving a hydrocolloid in powder form in water at high temperature or at boiling point and then cooled to room temperature. As the solution cools, enthalpically stabilized interchain helices may form from segments of individual chains, leading to a three-dimensional network. Examples for these type of hydrocolloids include gelatin and agar.

Heat-set gelation

In heat-set gelation, it requires the application of heat to gel formation. Examples for such systems include curdlan, methyl cellulose and starch. This technique is only applied when heat setting is required in foods (e.g. the use of starch in sauces). In heat setting mechanisms unfolding of native structures and their subsequent rearrangement into a network is taking place [3, 24].

Gel formation is a spontaneous process which can be either physically induced or chemically induced in a food system. Physically induced gelation could be achieved by controlling temperature and pressure. Chemically induced gelation occurs due to pH alterations and ionic strength. Heat-induced gelation which is achieved by controlling the temperature of the dispersion is the most prominent way of obtaining gels. Heat induced gelation is a two-step process. Supplying of energy causes unfolding of molecules to expose reactive sites. Then, higher molecular weight complexes are formed as a result of aggregation of these unfolded molecules [26]. Another factor that would affect on gelation would be pH. pH of a solution can be changed by addition of acids. pH alteration can change the net charge of the molecule. This would affect on the attractive and repulsive forces between molecules as well as the interactions between molecules and solvent. Thus, it would impact gelation. Another factor that determines gelation in a food system is the ionic strength. Monovalent and divalent cations such as sodium and calcium can increase the ionic strength of the gel. The electrostatic repulsive forces between the molecules are reduced or neutralised and gelation can occur. Ionic induced gelation is of greater importance in gels formed by hydrocolloids such as alginate, pectin or carrageenan [23].

Emulsification and surface active property

Emulsion is a mixture of two immiscible fluids where one phase is termed as the continuous phase and the other phase is termed as the dispersed phase [1]. Generally, dispersed phase is dispersed in the continuous phase as small spherical droplets. Oil-in-water and water-in-oil are the two main types of emulsions that are found in foods. Milk, cream, salad dressings, sauces and beverages are few food examples for oil-in-water emulsions while butter and margarine are two examples for water-in-oil emulsions. Other than that, there are some foods such as with other kinds of dispersed phases. For instance, gas bubbles are acting as the dispersed phase in whipped cream and ice crystals acts as the dispersed phase in ice cream [9]. Usually emulsifying agents are incorporated in to emulsions in order to maintain the proper texture and sensory attributes of these types of food products.

Emulsification and maintenance of emulsion stability by preventing this thermodynamically unstable emulsions breaking in to their constituent oil and aqueous phase is another important property exhibited by certain hydrocolloids. Emulsification property of hydrocolloids is utilized in food products such as carbonated soft drinks, ice creams, sauces and dressings. Among the hydrocolloids, most of them can act as stabilizing agents of oil-in-water emulsions. Since most hydrocolloids are not surface active, only few hydrocolloids can act as emulsifying agents [9]. Emulsification requires a substantial surface activity at the oil–water interface in order to facilitate the formation and stabilization of fine droplets during and after emulsification without coalesce [27]. Surface activity can be defined as the capacity to lower the tension at an oil–water interface. Gum Arabic, modified cellulose, pectins, modified starches and some galactomannans are the widely used polysaccharide based hydrocolloid emulsifiers in food industry [28]. Amphiphilic character of

a biopolymer is an essential character for that biopolymer to be surface active. Thus, the presence of hydrophobic groups is a key factor for a hydrocolloid to be an emulsifier. Thus, surface active behaviour of certain types of hydrocolloids may be due to the non-polar character of the chemical groups attached to the hydrophilic polysaccharide backbone such as hydrophobically modified starch/cellulose derivatives or the presence of a protein fraction linked covalently or physically to the polysaccharide [28].

Edible films and coating agents

At present, edible coatings and films have become popular among people. Hydrocolloids acts as ingredients in different coating and film formulations in food industry. Edible films or coatings can be defined as, thin layers of edible components which are used as primary packages of a food product and consumed with the food itself. Generally, edible films are self-standing structures in nature, while edible coatings adhere to the surface of the food component [29]. Hydrocolloids such as cellulose derivatives, starches, alginates, pectins, chitosans, pullulan and carrageenans are widely used as a main components in edible film and coating formulation. Other than that, proteineous hydrocolloids such as Soybean proteins, corn zein, gelatin, and whey are also used in coating and film formulation [30]. These films and coatings are mostly applied on foods to enhance the shelf life by maintaining the desirable quality of the products throughout the shelf life.

Properties of some common hydrocolloids

Gum Arabic

Gum Arabic can be introduced as one of the oldest and well-known hydrocolloid among all natural hydrocolloids. Gum Arabic readily dissolve in water and give a clear solution of very pale yellow to orange- brown with a pH around 4.5. Gum Arabic is Newtonian in behaviour with its viscosity being shear rate independent. Gum Arabic is a polyelectrolyte. Thus, the solution viscosity decreases in the presence of electrolytes due to charge screening and at low pH when the carboxyl groups become undissociated [31]. Gum Arabic exhibit a good emulsifying ability. Emulsifying ability of gum Arabic decreases with the increase in temperature while the emulsifying ability increases with the increase in gum concentration and stirring time. The water holding capacity range for gum Arabic obtained from *A. senegal* was 65.40–65.80 [31].

Pectin

Pectin is a linear polyuronide having a galacturonic acid backbone which is partially esterified with methanol and acetate. Aqueous solution of pectin is opaque to yellowish. There are high methoxyl pectin (HMP) and low methoxyl pectin (LMP). HMP is cold water soluble while LMP only soluble as Na or K salt. Pectin is a

commonly used gelling agent in the food industry. Required gelling agent concentration for LMP is 0.1–4% w/w while it is 2–4% w/w for HMP. LMP forms thermo-reversible gels in the presence of divalent cations such as Ca at low pH (3–4.5) while HMP form thermo-irreversible gels at high solid levels and low pH values [1].

Starch

Starch is commonly used as a thickening agent in food industry. Starch is composed of amylose and amylopectin. Starch is comprised of a lot of hydroxyl groups on the backbone, thus can be modified in to starch derived semi-synthetic hydrocolloids by incorporating functional groups [32]. Starch is insoluble in cold water and soluble in hot water. Dissolution of starch forms turbid suspensions that sediment at room temperature. Viscosity of a starch solution in water is low at room temperature while starch gelation takes place when heating. When the temperature of the starch solution exceeded 60 °C, starch granules swell and gelation takes place resulting heat-stable gels in water. Shear stability and pH stability of starch is low after gelation. Decomposition of starch takes place when cooking in acidic or alkaline systems ($6 > \text{pH} > 8$), oxidation by free radicals, at high shear forces and when exposed to certain enzymes. Gel transparency of starch gels is low and syneresis in gels is high. Preferred dosage of starch to be incorporated in food is around 1–5% [33].

Locust bean gum

Locust bean gum is a popular stabilizer and a thickening agent. Locust bean gum partially soluble in cold water. A solubility of around 70–85% is shown in water when heated to 80 °C for 30 min. Maximum viscosity of locust bean gum can be obtained by hydration for about 2 h. [34] shows a non-Newtonian behaviour at high shear rates, but exhibits Newtonian flow behaviour at low shear rates. Intrinsic viscosity and molecular weight is lower compared to other galactomannan like guar and tara galactomannan. Locust bean gum shows a power law exponent ' α ' of 0.77 of Eq. 1 when water is used as the solvent [34]. Generally, locust bean gum does not form gels under normal conditions but has a possibility to form a weak gel by applying a freeze–thaw treatment. It also forms gel in the presence of large amount of sucrose and maximum gel strength could be obtained by 45% w/w fructose, 50% w/w sucrose or sorbitol, and 55% w/w glucose [35]. Gel strength could be increased by blending locust bean gum with other gums like xanthan gum, k-carrageenan, etc. [34]. Locust bean gum shows high sorption heat of about 27 kJmol⁻¹ which exhibits the less hygroscopicity of the gum [36].

Guar gum

Guar gum is commonly used as a thickener in the food industry. Guar gum swells and/or dissolves in polar solvent on dispersion and form strong hydrogen bonds while it forms weak hydrogen bonds on nonpolar solvents. Guar gum is stable over a pH range of about 1.0–10.5 with fastest hydration at pH 8–9 and slowest at pH above 10 and below 4. Guar gum exhibits a pseudoplastic or shear-thinning behaviour in

aqueous solutions thereby reducing the viscosity with increasing shear rate. It also gives highly viscous solutions by rapidly hydrating in cold water. Complete hydration of guar gum yields a thixotropic rheological system. Viscosity of a guar gum solution is governed by temperature, pH, ionic strength, gum concentration used and type of agitation. Temperature range of 25–40 °C is desirable to reach maximum viscosities of guar gum dispersions. Generally, guar gum exhibits a Newtonian behaviour up to 0.5% concentration whereas at concentrations above 0.5% it shows a non-Newtonian behaviour and thixotropic systems. Incorporation of below 1% of guar gum is best suited in food products [37].

Konjac mannan

Konjac mannan is found in tubers of Konjac (*Lasioideae Amorphophallus*). Gelation of konjac mannan is induced by deacetylation. Deacetylated konjac glucomannan which is used to form thermos-irreversible gels is obtained by alkaline processing of konjac glucomannan. With the increase of deacetylation, gelation viscosity and elastic modulus will increase. Deacetylation of konjac glucomannan causes the konjac glucomannan molecular chain to change from semi-crimping to self-crimping which leads to self-aggregation between the konjac glucomannan molecules under heating conditions [38]. The lowest critical concentration of aqueous solution of konjac flour necessary for gel formation is about 0.5% [39].

Xanthan gum

Xanthan gum is popular as a thickener in the food industry. Xanthan gum is highly soluble in cold and hot water. Xanthan solutions are pseudoplastic, or shear thinning. Xanthan gum is highly viscous even at low polymer concentrations. Viscosity depends on the biopolymer concentration, temperature, pH and concentration of salts [40].

Carrageenan

Carrageenan consists of different types as λ , κ , ι , ϵ and μ . Aqueous solutions of carrageenan are opaque. All the above-mentioned carrageenan types are soluble in hot water while λ -Carrageenan and κ -carrageenan are soluble in cold water [1]. After dissolution, carrageenan forms highly viscous solutions. Viscosity may range between 30 and 300 cp [41]. Viscosity of the solution depends on temperature, concentration, presence of other solutes, type of carrageenan and molecular weight. Viscosity increases with the increases concentration and decreases with the increase of temperature. Depolymerisation of carrageenan occurs during acid catalysed hydrolysis and complete loss of carrageenan functionality occurs at elevated temperatures and low pH values. Carrageenan is stable within the pH range 5–10 [1]. Under proper conditions, κ -carrageenan and ι -carrageenan form thermo-reversible sol–gels. The gelling point of carrageenan may vary from 30 to 50 °C [41]. Gel strength ranges from 100 to 350 g/cm². λ -carrageenan does not form gels. Concentration of carrageenan preferred in food products ranges from

Fig. 2 Carrageenan extracted from *kappaphycus alvarezii*



Fig. 3 Agar extracted from *Gracilaria edulis*



0.005 to 2.0% by weight [42]. Carrageenan which was extracted from *kappaphycus alvarezii* before oven drying is shown in Fig. 2.

Agar

Agar is comprised of two basic polysaccharides as agarose and agaropectin. Agarose is the prominent polysaccharide among the two which is about 70% of the mixture [1]. Aqueous solutions are opaque and yellowish. Insoluble in cold water while soluble in hot water may be above 80 °C [1]. Viscosity of a solution may vary between 10 and 100 cp (41). Highly tolerant to temperature. Highly soluble in concentrated sugar solutions [1]. Agarose is responsible for gelling property of agar while agaropectin is responsible for thickening property [41]. Gel formation takes place on cooling and it is thermo-reversible [9]. Gelling point may vary from 32 to 45 °C, act as a gelling agent at concentrations 0.5–2% w/w [41]. During gelation, molecules undergo a coil-helix transition which is followed by aggregation of helices. Gel strength can be between 700 and 1000 g/cm² [9, 41]. Levels of around 0.5–2% are utilized in food products [1]. Agar which was extracted from *Gracilaria edulis* before oven drying is shown in Fig. 3.

Alginate

Alginate is a polysaccharide which is extracted mainly from brown algae species. Alginate is soluble in water (except pure alginic acid and calcium alginate), forms aqueous solutions of opaque and brownish yellow after dissolution. Solutions exhibit pseudoplasticity (shear thinning) property due to parallel arrangement of linear molecule chain. Decomposition of alginate takes place by acid ($\text{pH} < 5$), alkaline ($\text{pH} > 9$), free radical oxidation and enzymes. Alginate form thermo-irreversible gels in the presence of divalent cations such as Ca^{2+} at low temperatures and pH values. Gels exhibit a high gel strength which is stable during cooking. Gel formation can be controlled by controlling the release of divalent cations or acids in to the medium. Gels exhibit syneresis over storage time. Levels of 0.7–2% are preferred in foods [33]. Alginate which was extracted from *Sargassum sp.* before oven drying is shown in Fig. 4.

Gelatin

Gelatin is popular as a gelling agent in the food industry. Gelatin is derived from the parent protein collagen. Collagen containing tissues such as skins and bones of porcine, fish and bovine are used to obtain gelatin [9, 43]. Gelling temperature, melting temperature and solubility for mammalian gelatin 220 g bloom are 26–27 °C, 33–34 °C and greater than 40 °C, for cold fish gelatin are 4–8 °C, 14–16 °C and greater than 22 °C, for warm water fish gelatin are 21–22 °C, 28–29 °C and greater than 35 °C [9]. Bloom value of gelatin is a measure of the strength or the rigidity of the gelatin gel formed which is measured under standard conditions. The Bloom values of commercial gelatins are in the range of 50–300 g Bloom. A higher Bloom value of gelatin represents a higher gelling and a melting temperature and a stronger gel. The gelatins are classified as high-Bloom (200–300 g), medium-Bloom

Fig. 4 Alginate extracted from *Sargassum sp.*



(100–200 g) and low-Bloom (50–100 g) [44]. Generally, gelatin forms thermo-reversible viscoelastic gels upon cooling. During gelation, a polypeptide chain takes an orientation to induce a reactive site. Later, condensation of two other chains near the reactive site occurs giving rise to triple helix formation, have a high water binding capacity. Gelling concentration is from 1 to 5% w/w. Dosage concentration preferred in food for effective functional properties is 0.1% [1].

Chitosan

Chitosan is a natural, biodegradable and a non-toxic hydrocolloid [45]. It is a water-soluble derivative of chitin. Chitosan is insoluble at higher pH ranges and dissolves easily at low pH conditions. Chitosan is insoluble in organic solvents. Chitosan also exhibits an antimicrobial property. It also exhibits mucoadhesive properties in vitro. Chitosan forms thermo-reversible gels by aggregation of chitosan chains through hydrophobic bonding [1, 45].

Carboxymethyl cellulose (CMC)

Anionic long chain linear polymer water soluble exhibit a high viscosity but viscosity will be reduced with the addition of electrolyte and at low pH. CMC is physiologically inert, non-caloric, odourless and tasteless. It forms clear solutions without any cloudiness [46].

Methyl cellulose

Methyl cellulose is the simplest cellulose derivative hydrocolloid. Viscosity of a methyl cellulose solution increases with the increase of temperature above a critical temperature point 29 ± 2 °C and may form a thermo-reversible gel, thus classified as a lower critical solution temperature polymer (LCST). Viscosity of a methyl cellulose solution is not affected by the addition of electrolytes or with the pH [47].

Hydroxypropyl methyl cellulose

Viscosity of a hydroxypropyl methyl cellulose solution increases with the increase of temperature (gelation may occur). Viscosity of such a solution is not affected by the addition of electrolytes or with the pH [9].

Applications

Applications and functions of common hydrocolloids which are used in the food industry are tabulated in the Table 2.

Table 2 Functions and applications of hydrocolloids in food industry

Hydrocolloid	Function	Application in food industry	References
Gum Arabic	Act as an emulsifying agent Can be used as a stabilizer and a thickener Impart a smooth texture to frozen foods by inhibiting the formation of ice crystals Improves consistency and shelf-life	Juices, beverages (by acting as an emulsifier in juices and beverages, gum Arabic provides a better flavour, turbidity and colour) Soft drink syrups, creams, sticky confections Frozen foods Confectionary items such as, marshmallows and pastilles, Beverages, purees, spreads Fruits and vegetables such as apples, bananas, mushrooms	[9, 31, 48]
Pectin	Used as an ingredient in edible coatings and films to enhance the shelf life of fruits and vegetables. Application of an edible coating in fruits will reduce weight loss, loss of firmness, and delay the changes of titratable acidity, colour, total soluble solids and pH Act as a microencapsulator	Freeze-dried strawberry powder, oleoresin such as cumin and cardamom, polyphenols Jam, jujubes, jelly, marmalade, yogurt, ice creams Fruits and vegetables Certain drugs Baked foods flavours	[1, 33]
Starch	Gelling agent, thickening agent and a stabilizer Coating agent Used as an encapsulating agent Fat replacer Encapsulating agent Thickening agent Texture improver in dairy products and in chewy products Gel consistency improver Improve the stability Stabilizer and a thickener	Sauces, spreads, dressings, soups, condiments, gravies Dairy products like yogurt, puddings, Sauces, spreads, dressings, confectionery Fillings and dough of bakery products Beverages, ice cream, Low-fat yoghurt	[1, 33]
Locust bean gum			[34]

Table 2 (continued)

Hydrocolloid	Function	Application in food industry	References
Guar gum	Incorporation of locust bean gum in to the dough will improve the final texture and improves the viscosity of the dough	Bakery products such as breads, cookies, biscuits, (wheat flour-based bakery products and gluten-free products), Noodles fresh fruits, vegetables and meat products Yoghurt Wheat flour based bakery products, tomato ketchups Chapati, bread, cake, rice flour-based pasta, yoghurt Chapati, bread Ice cream Ketchups Chapati, bread, sausages Frozen food products, sauces, salads	[37, 49–51]
	Increase the bakery product volume and retard the aging of bakery products		
	Improvement of the water absorption capacity and the wheat flour dough development time		
	Act as an alternative binding agent for gluten in gluten free products		
	Addition of the gum in noodles dough improve the dough rheology and the textural properties of the cooked noodles		
	Improvement in textural properties of noodles is mainly due to the strengthening effect of locust bean gum on the gluten network		
	Addition of locust bean gum reduces the cooking loss and swelling index of noodles		
	Used in edible films and coatings. Locust bean gum-based edible films and coatings can act as carriers of certain bioactive compounds to foods		
	Stabilizer, thickener		
	Fibre source		
Texture improver			
Dough improver			
Formation of small ice crystals			
Consistency improver			
Improves the softness of foods			
Act as a binder			

Table 2 (continued)

Hydrocolloid	Function	Application in food industry	References
konjac mannan	Thickening agent	Puddings, ketchups, juice drinks, sauces and dressings	[33, 38, 39]
	Texture improver	yoghurt, pasta, confectionery, jelly, meat, low fat processed cheese	
	Moisture enhancer	meat, seafood	
	Gelling agent	Confectionary industry, jellies	
	Improve the mouthfeel	puddings and beverages	
	Fibre source	Noodles, pasta	
	Bulking agent	Noodles, pasta, meat	
	Used as a component in edible films	Edible films for fruits	
	Fat replacer	Meat and dairy products, low fat yogurt, mayonnaise	
	Moisture enhancer	Confectionery	
	Binding agent	Restructured meat, pasta, vegetable products, desserts	
	Clarifying agent	Fruit juices, alcohols	
	To reduce oil uptake	fried products	
	Thickener	Salad dressings, sauces, syrups, relishes, toppings	
	Emulsion stabilizer	Dairy products, salad dressings, beverages	
Xanthan gum	Suspending agent	Beverages, salad dressings	
	Provide a uniform viscosity	Sauces	
	Improve freeze–thaw stability	Frozen foods	
	Facilitates pumping	Baked goods, rice breads	
	Dispersant	Salad dressings	
	Incorporated to prevent sedimentation of fruit or chocolate pieces before and during drying	Cake	
	Increase the volume and retard staling		
	To achieve a consistent particle distribution	Instant dry mix, soups, beverages, desserts	

Table 2 (continued)

Hydrocolloid	Function	Application in food industry	References
Carrageenan	Gelling agent	dairy desserts like puddings, milk shakes, ice cream and chocolate milk	[1, 20, 41, 42]
	Thickening agent	Sauces	
	Stabilizer	Dairy products	
	Film and coating formulating agent	Edible films and coatings for fruits, cheese, vegetables	
	Encapsulating agent	Certain drugs	
	Crystallization inhibitor	Ice cream	
Agar	Binding agent	Processed meats, infant food formulations, dietetic formulations	
	Provide a uniform consistency for food products	Soy milk, dairy products, chocolate and other flavoured milks, nutritional supplement beverages and infant formulas	
	Gelling agent	Fruit candies, jellies, jams, custard puddings	[1, 20, 23, 33, 41]
	Encapsulating agent	Certain types of drugs	
	Used in coating and film formulations	Coatings and films used for fruits, vegetables, meat and fish	
	Stabilizer	milk shakes, ice cream, bakery icings	
	Maintain structural integrity in foods	Frozen foods, cakes	
	Fining agent	Act as a fining agent to clarify wine, juice and vinegar	
	Incorporated as a vegetarian gelatin substitute	Jellies, Japanese desserts	
	Stabilizer	Drinks, jelly, ice cream, desserts, instant pudding mixtures, baked goods, frozen foods, mayonnaise, salad dressings, processed cheese, dairy products, pie, pastry filling, dessert gels, cold prepared bakery creams	[1, 20, 41]
Alginate	Thickening agent	Soups	
	Act as a component in coating and film formulations	Coatings and films used for fruits, vegetables, meat and fish	
	Encapsulation	Prebiotics, flavours, and functional food oil	
	Used as a texture improver	Desserts, fruit gummies, pastilles, yogurt	[1, 43, 44, 53]

Table 2 (continued)

Hydrocolloid	Function	Application in food industry	References
Chitosan	Gelling agent	Desserts, fruit gummies	
	Encapsulating agent	Essential oils	
	Foam stabilizer	Marshmallows, caramels	
	Binding agent	Pastilles, broths and canned meats	
	Stabilizer	In confectioneries, meat and sausages	
	Edible coatings and films	Fruits and vegetables	
	Stabilisation of syneresis	Yogurt	
	Emulsion stabilization	Meat and sausages	
	A component in edible coatings and films	Food packaging, antimicrobial films and coatings	[1, 16, 45, 54]
	Used as a component in non-medical products	Fat binder in cholesterol lowering and slimming formulations	
Used as an encapsulating agent	For drug delivery, essential oils, flavours, vitamins, antioxidants, and probiotics		
Possesses an antimicrobial property	Chitosan is a promising ingredient to be used in edible coatings and films used to preserve the microbial quality of foods		
Function as an active ingredient in lowering the concentration of inorganic phosphorous to be incorporated in to foods	Cheese, fish paste, juices, noodles, desserts		
CMC	To reduce oil uptake in fried products	Fried products	[9, 22, 46, 52]
Act as an emulsion stabilizer	Beverages, dairy products, frozen products like ice creams		
Act as a textural improver in various food items	Frozen products		
Act as a moisture binder	Frozen desserts		
Incorporate in foods to improve sensory attributes by preventing gravitational separation of suspended particles	Beverages		
Methyl cellulose	Syneresis inhibitor	Yogurt	[8, 9, 45, 47, 55]
	Act as a thickener	Mayonnaise, dressings, creams and sauces	
	Act as an emulsifier	Cheese, frozen foods, peanut butter	

Table 2 (continued)

Hydrocolloid	Function	Application in food industry	References
	Texturing agent	Bakery products, ice cream, pasta, gluten free products	
	Prevent separation of two mixed liquids	Juices	
	Control emulsion stability, viscosity, and reduce fat and egg content	Mayonnaise, creams, sauces, dressings	
	Stabilization of foams	Cold drinks	
	Reduce the ice crystal growth during freezing and thawing	Ice cream	
Hydroxypropyl methyl cellulose	Predust agents	Battered fish nuggets	[8, 56]
	Dietary fibre source	Cake	

Marketed product of some common hydrocolloids

At present, the market share of hydrocolloids is exhibiting a growing trend. The market value for hydrocolloids is estimated to reach USD 7.56 billion by 2020 [2]. At present, seaweed-derived hydrocolloids have a global market value of approximately USD 1.1 billion, which is forecasted to increase. Among them, agars have the highest retail price per kg which is approximately USD 18. Among the seaweed hydrocolloids, carrageenan has the highest commercial total production of 60,000 ton/year and contribute to the highest total market value of USD 626 million per year [57]. It is also stated that the global market value for alginates is estimated to be USD 339 million/year. At present, the alginates market share by application in food industry and pharmaceutical industry has increased by 20%. The physicochemical properties of the marketed carrageenan, agar and alginate product are given in the following Table 3. The global market for pectin in 2015 was approximately USD 958 million with an annual growth rate of 7.3% during 2018–2023. The largest market for pectin in 2018 was in Europe which is around 31,000 metric tons that worth USD 420 million [58]. The marketed products of pectin can be stored in room temperature, soluble in pure water, has a neutral to fruity smell and has an appearance of white to light brown colour. The reported sales and market value for gum Arabic in 2002 were approximately 50,000 tons and USD 101 million which account for 3% of the global hydrocolloid market [59]. Marketed product of gum Arabic is available as white to yellowish-white flakes, powder, granules roller-dried or spray-dried materials, dissolve in water and insoluble in ethanol. Guar gum is also a widely used hydrocolloid in the food industry. India is considered as the leading producer of guar gum that accounts for 80% of the total guar gum production in the world [37]. India export guar gum to more than 100 countries worldwide. In 2017, India has exported USD 248.53 million worth guar gum to USA which is accounted for 52.3% of the total exports. The second largest export market for Indian guar gum is Norway which worth USD 34.67 million in 2017 that account for 7.3% of the market [37]. The marketed product of food grade guar gum for the food and pharmaceutical industry has particle size of 100 MESH with the viscosity 3000–6000 cps and particle size of 200 MESH with the viscosity 2000–9000 cps. Xanthan gum is another commonly used gum in the food industry. Considering the demand for Xanthan gum in various

Table 3 Physicochemical properties of marketed carrageenan, agar and alginate

Property	Carrageenan	Agar	Alginate	References
Solubility	Hot water	Hot water	Hot water	[41, 57]
Viscosity (cP) of 1.5% solution at 60 °C	10–100	30–300	–	
Melting point	50–70 °C	85–95 °C	Greater than 300 °C	
Colour of the marketed product	Yellowish powder	Yellowish powder	Yellowish powder	

sectors, 86 000 tons of xanthan gum are produced every year at a cost of around USD 400 million per year. It is stated that from the total volume of the global production of xanthan gum, 65% is used by the food industry [60]. Marketed product of xanthan gum is normally cream white in colour, particle size of 80 MESH product can make solutions with viscosities more than 1200 cps while particle size of 200 MESH product can make solutions with viscosities more than 1400 cps. Among cellulose derivative hydrocolloids, carboxymethyl cellulose was identified as the first cellulose ether, which gained economic and industrial importance starting from 1920. Additionally, among cellulose derivative hydrocolloids, carboxymethyl cellulose ranks top in sales with more than 230,000 tons of annual sales volume, which is expected to increase every year [61]. Even though carboxymethyl cellulose is the prominent cellulose derivative used in the food industry, cellulose derivatives such as methyl cellulose and hydroxypropyl methyl cellulose can also be used in the food industry as hydrocolloids. Possible applications of methyl cellulose and hydroxypropyl methyl cellulose are given in Table 2. Marketed product of methyl cellulose produces clear, viscous, opalescent colloidal solutions in water and insoluble in ethanol or chloroform.

Conclusion

Hydrocolloids are a valuable group of additives that provide functions such as thickening, emulsifying, stabilizing, fat replacing, flavour encapsulating, edible coating and acting as gelling agents in a wide array of food systems. At present, consumer preference is more towards natural hydrocolloids mainly due to their non-toxicity, biocompatibility and eco-friendliness. However, semi-synthetic hydrocolloids which could be considered as stronger emulsifiers, non-toxic and less likely to undergo microbial growth have synthesized by chemically or physically modifying natural hydrocolloids alleviating certain disadvantages of natural hydrocolloids. Thus, semi-synthetic hydrocolloids could be preferred over synthetic hydrocolloids. Guar gum, locust bean gum, gum Arabic, xanthan gum, carrageenan, agar, alginate, gelatin, pectin, carboxymethyl cellulose, methyl cellulose and hydroxypropylmethyl cellulose are commonly used as thickeners, gelling agents and stabilizers in food products. Gum Arabic is the only naturally derived hydrocolloid emulsifier utilized in food industry. Other than that, most of these hydrocolloids have shown promising applications in development of edible coating and film formulations which are utilized in food industry to enhance the quality attributes of food products.

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