

Paper No.: 13

Paper Title: FOOD ADDITIVES

Module – 09: Stabilizers, Thickeners and Gelling agents for the food industry

Colloids, hydrocolloids and *gums* are the substances, which indicate that these materials are macromolecules, mostly polysaccharides (molecular weight 10^5 - 10^6), that are capable of interacting with water.

Hydrocolloids are defined as ‘a macromolecular substance such as a protein or polysaccharide which swells by absorption of water, in some cases forming a stiff gel’ (Ockerman 1978). Food gums are usually added to food systems/products for specific purposes, such as thickening agents, stabilization, gelling, etc. Hydrocolloids ultimately alter the rheological properties in a desired fashion for food systems.

Ideal characteristics of a food grade stabilizer

- ✚ Should be nontoxic
- ✚ Should readily disperse in the mix
- ✚ Should not produce excessive viscosity or separation or foam in the mix
- ✚ Should not clog strainers and filters
- ✚ Should not impart off flavor to the product
- ✚ Should be economical

Types of stabilizers

There are a variety of hydrocolloids on the market, including those derived from plants or seaweed, and those produced by microorganisms. In general, hydrocolloids have a sugar backbone that contains protruding substituents such as esters, sulfates, or additional sugars. Hydrocolloids available for food applications are either neutral or negatively charged.

Examples of commonly used stabilizers in the food industry are discussed in depth herein.

I. Gelatin (E441)

Gelatin is a proteinaceous material obtained from animal connective tissue (collagen) using hydrolysis in acidic (type A) or basic (type B) solution followed by hot water extraction. Commercially, skins or bones of different animal species, such as beef, pork, fish and poultry, form the main raw material for gelatin production. It hydrates readily in warm or hot water to give low-viscosity solutions that have good whipping and foaming properties. After cooling, the network of polypeptide chains associates slowly to form clear, elastic gels that are syneresis free. This relatively expensive stabilizer is effective at concentrations of 0.3–0.5%; however, it may not prevent the effects of heat shock. It is also not acceptable to certain religious and vegetarian populations. The use of gelatin as a stabilizer produces thin mixes that require a long aging period. Gelatin disperses easily and does not cause wheying-off or foaming.

II. Galactomannans

Guar gum and locust bean gum (LBG), both classified as galactomannans with the same mannose backbone, are used in products such as cheeses, frozen desserts, processed meats, and bakery products. However, these two galactomannans differ in cold water solubility as well as in their gelling capability due to their difference in the degree of substitution and the distribution of side units.

Guar gum (E412): Guar gum is extracted from the seeds of a tropical legume, *Cyamopsis tetragonoloba*, which is milled in order to obtain guar gum. Guar gum is a neutral hydrocolloid with linear chains of D-mannopyranosyl units with D-galactopyranose substituents protruding by (1→6) linkages. For every galactose residue there are approximately two mannose residues. Guar gum is highly substituted which allows for good hydration and hydrogen bonding activity. The molecular weight (MW) of guar gum is between 220,000 and 300,000. Guar gum has a higher degree of galactose substitution (40%) than locust bean gum (20-23%). On an average, for every two molecules of mannose, a galactose side unit is attached. Guar gum is stable over a wide range of pH, with its optimal rate of hydration between pH 7.5-9.0.

Locust bean gum /Carob bean gum) (E410): Locust bean gum (LBG), also called ‘carob bean gum’ is obtained from the beans of the tree *Ceratonia siliqua*, grown mostly in the

Mediterranean area. The slightly off-white powder consists of 88% galactomannan, 3-4% pentosan, and 5-6% protein, cellulose and ash. The molecule weight of locust bean gum is approximately 310,000. LBG is only partially soluble in cold water and it must be heated above 85°C to hydrate fully. LBG on an average has four molecules of mannose to one galactose side unit. LBG is a neutral galactomannan with linear chains of 1,4- linked β -D-mannan backbone with 1,6-linked α -D-galactose side units. For every galactose residue there are approximately 4 mannose residues. At ambient temperatures, LBG is only partly soluble therefore heat treatment is required for maximum solubility. Since LBG is a neutral hydrocolloid it is stable over a wide pH range (3-11).

III. Carrageenan (Irish moss) (E407)

The red seaweed family, *Rhodophyceae*, provides the polysaccharides agar, carrageenan, and furcellaran. The main species of *Rhodophyceae* include *Euchema cottonii* (now called *Kappaphycus alarezii*) and *Euchema spinosum* (now called *E. denticulatum*) from which carrageenan gum is extracted. *E. cottonii* produces κ -carrageenan (< 10% iota), *E. spinosum* yields ι -carrageenan (< 15% kappa), and *Chondrus crispus* yields both κ - and λ -carrageenan. Individual plants that grow together will produce both types of carrageenan. Carrageenan gum, a negatively charged hydrocolloid has a linear backbone of repeating galactose units with different proportions and locations of ester sulfate groups and 3,6- anhydrogalactose (anhydro bridges).

The number of ester sulfate groups and anhydro bridges present on the backbone distinguishes kappa, lambda, and iota carrageenan from one another. The sulfate groups make the carrageenan molecule more water soluble, whereas the anhydro bridges inhibit water solubility. κ -carrageenan has one sulfate group and one anhydro bridge for every two galactose molecules. ι -carrageenan has a similar structure; however it possesses an additional sulfate group, making ι -carrageenan more water soluble than kappa. Lambda, which is the most water soluble of the three, consist of three sulfate groups and no anhydro bridges for every two galactose molecules.

Table 1. Content of ester sulfate and anhydro bridges in carrageenan

Carrageenan type	Ester sulfate	Anhydro bridges
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κ -carrageenan	25%	34%
$\acute{\iota}$ -carrageenan	32%	30%
λ -carrageenan	35%	Little or nil

All carrageenan types are hot water soluble. Lambda carrageenan produces a viscous solution, which exhibits pseudoplastic characteristics when it is pumped or stirred. Usually it is used for thickening in order to provide body to a product. κ - and $\acute{\iota}$ -carrageenan is capable of forming a range of gel textures upon cooling of a hot solution. The gel textures depend on the cations (Ca^{++} , K^+ , NH_4^+) used to induce gelling. The gels are thermally reversible, as they remelt 5-20°C above the gelling temperature and re-gel upon cooling.

IV. Gum Arabic (E414)

Gum Arabic (Acacia gum) is a natural, vegetable exudate from acacia trees (primarily in Africa). The main chain of this polysaccharide is built from (1→3) and (1→6)-linked β -D-galactopyranosyl units along with (1→6)-linked β -D-glucopyranosyl uronic acid units. Side branches may contain α -L-rhamnopyranose, β -D-glucuronic acid, β -D-galactopyranose, and β -L-arabinofuranosyl units with (1→3), (1→4), and (1→6) glycosidic linkages. Gum arabic has a high water solubility (up to 50% w/v) and relatively low viscosity compared to other exudate gums.

V. Agar (E406)

Agar constitutes another group of polysaccharides from red-purple algae of the *Rhodophyceae* class. Agar is a linear polysaccharide built up of the repeating disaccharide unit of (1→3)-linked β -D-galactose and (1→4)-linked 3,6-anhydro- α -L-galactose residues. In contrast to carrageenans, agar is only lightly sulphated and may contain methyl groups. Agar is a thermo-reversible gelling polysaccharide, which sets at 30 to 40°C. Being less sulphated than κ - and $\acute{\iota}$ -carrageenans, agar can form strong gels, which are, subject to pronounced syneresis, attributed to strong aggregation of double helices. The ability to form reversible gels by simply cooling hot, aqueous solutions is the most important property of agar. The high melting point of agar gels is improved by the addition of salts.

VI. Xanthan (E415)

This bacterial exopolysaccharide is obtained by the growth of *Xanthomonas campestris* in culture. Xanthan gum is produced by the process of submerged aerobic fermentation using glucose as the primary carbohydrate source. The xanthan gum is recovered, purified, dried and milled into a white powder. Xanthan gum is an anionic (negatively charged) linear hydrocolloid with a (1→4) linked β -D-glucose backbone. The side unit, a trisaccharide, contains a glucuronic acid residue linked (1→4) to a terminal mannose unit and (1→2) to a second mannose which connects to the glucose backbone. Generally, xanthan gum is stable over the pH range 2 to 12. The functionality of xanthan gum is highly dependent on the ionic strength of the solution.

Xanthan gum is an excellent thickening agent. It exhibits pseudoplastic rheological characteristics (i.e. as shear is increased, viscosity gets reduced). Its blend with guar gum and/or LBG, it makes an effective stabilizer for ice cream, ice milk, sherbet, and water ices. A combination of xanthan gum with sodium alginate is reported to serve as a milk shake stabilizer.

VII. Alginates

Alginates constitute the primary structural polysaccharides of brown seaweeds (*Phaeophyceae*). Alginates, or algin, are a generic term for the salts and derivatives of alginic acid (E400). Alginates are unbranched copolymers of (1→4)-linked β -D-mannuronic acid (M) and α -L-guluronic acid (G) residues. If the uronic acid groups are in the acid form (–COOH), the polysaccharide, called alginic acid, is water insoluble. The sodium salts of alginic acid (–COONa), sodium alginates (E401), are water soluble. Alginates dissolve in cold water and gel in the presence of calcium and acid.

VIII. Gellan gum (E418)

Gellan gum is a fermentation polysaccharide produced by the microorganism *Sphingomonas elodea*. The molecular structure of gellan gum is a straight chain based on repeating glucose, rhamnose and glucuronic acid units. Upon cooling of gellan solutions, the polysaccharide chains can assume double helices, which aggregate into weak gel structures. In the presence of

appropriate cations (Na^+ or Ca^{++}), the double helices form cation-mediated aggregates, which leads to formation of strong gel networks.

IX. Cellulose and its derivatives

Microcrystalline cellulose (E460): Microcrystalline cellulose (MCC) is prepared by treating natural cellulose with hydrochloric acid to partially dissolve and remove the less organized amorphous regions of this polysaccharide; end product consists of crystallite aggregates.

Carboxymethyl cellulose (E466): Carboxy methyl cellulose (CMC) is an anionic, water-soluble polymer capable of forming very viscous solutions. CMC is prepared by first treating cellulose with alkali (alkali cellulose), and then by reacting with monochloroacetic acid. The degree of substitution (DS) with the carboxyl groups is between 0.6 to 0.95 per monomeric unit (maximum DS being 3). CMC like guar gum, is soluble in either cold or hot water. Dispersions of the gum show shear thinning properties, but products of lower DS are thixotropic and viscosity decreases with increase in temperature. Other cellulosic colloids include methyl cellulose (MC – **E461**) prepared by treating alkali cellulose with methyl chloride; and hydroxypropylmethyl cellulose (HPMC – **E463**) prepared by treating cellulose with mixture of methylene chloride and propylene oxide. Unlike CMC, they form weak gels on heating when the temperature rises $> 52^\circ\text{C}$ for MC and $63\text{--}80^\circ\text{C}$ for HPMC.

Sodium-carboxymethyl cellulose (**E466**) is a chemically modified natural gum is a linear, long-chain, water-soluble, and anionic polysaccharide. Purified Na-CMC is a white to cream colored, tasteless, odorless, free-flowing powder.

X. Pectins (E440)

Commercial pectins are prepared mostly from some by-products of the food industry, such as apple pulp, citrus peels, and sugarbeet pulp. Pectins are the most complex class of plant cell wall polysaccharides. They comprise of two families of covalently linked polymers, galacturonans and rhamnogalacturonans. The carboxylic acid groups in galacturonans may be methyl esterified. Based on the degree of esterification, pectins are divided into two categories: low methyl (LM) pectin that contains less than 50.0% methyl esters, and high methyl (HM) pectin with more than 50.0% methyl esters. Pectin as extracted normally has $> 50\%$ of the acid units esterified and is

referred to as ‘**High methoxyl pectin**’ (**HMP**). Some pectins are treated during manufacture with ammonia to produce **amidated pectins (i.e. low methoxyl pectin)**, which have particular advantages in some applications.

XI. Starch and Modified Starches

Starch is a polysaccharide carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. It comprises of amylose and amylopectin as its macromolecules. In the unmodified form, starches have limited use in the food industry. In general, native starches produce weak-bodied, cohesive, rubbery pastes when heated and undesirable gels when the pastes are cooled. The properties of starches can be improved by various modifications.

The examples of such modified starches are: Acid-treated starch (**E1401**), Alkaline-treated starch (**E1402**), Bleached starch (**E1403**), Oxidized starch (**E1404**), Starches, enzyme-treated (**E1405**), Monostarch phosphate (**E1410**), Distarch glycerol (**E1411**), Distarch phosphate esterified with sodium trimetaphosphate (**E1412**), Phosphated distarch phosphate (**E1413**), Acetylated distarch phosphate (**E1414**), Starch acetate esterified with acetic anhydride (**E1420**), Starch acetate esterified with vinyl acetate (**E1421**), Acetylated distarch adipate (**E1422**), Acetylated distarch glycerol (**E1423**), Hydroxypropyl starch (**E1440**), Hydroxypropyl distarch phosphate (**E1442**), Hydroxypropyl distarch glycerol (**E1443**), Starch sodium octenyl succinate (**E1450**).

Modified starches consist of starch with low to very low level of substituent group. Enzymatic modification of starch is hydrolysis of some part of starch into a low molecular weight of starch called maltodextrin, or dextrin using amylolytic enzymes. They are widely used for food industries. Physical modification involves pre-gelatinization, and heat-treatment of starch, etc. Pre-gelatinized starches are pre-cooked starches that can be used as thickener in cold water. While the heat-treatment processes include heat–moisture and annealing treatments, both of which cause a physical modification of starch without any gelatinization, damage to granular integrity, or loss of birefringence. Chemical modification (viz., acid/alkaline treated, oxidized, etc.) is the mainstream of the modified starch in the last century.

Thickening and gelling agents

Hydrocolloids are frequently used in several foods for '*thickening*'. The process of thickening involves the nonspecific entanglement of conformationally disordered polymer chains; it is essentially a polymer-solvent interaction. Hydrocolloids that have been used as thickening agents in various food systems include starch, modified starch, xanthan, galactomannans like guar gum and LBG, gum Arabic or acacia gum, gum karaya, gum tragacanth and CMC.

'Gels' may also be defined as a form of matter intermediate between solid and liquid and show mechanical rigidity. They consist of polymer molecules crosslinked to form tangled and interconnected molecular network immersed in a liquid medium, which in food system is water. Hydrocolloids form gels by physical association of their polymer chains through hydrogen bonding, hydrophobic association and cation mediated cross-linking and differ from synthetic polymer gels, which normally consist of covalently cross-linked polymer chains. Hence, hydrocolloid gels are often referred to as 'physical gels'. The important gums that find application in food as gelling agents include alginate, pectin, carrageenan, gellan, gelatin, agar, modified starch, methyl cellulose and HPMC.

Choice of a stabilizer

Decisions regarding choice of a stabilizer may be based on following parameters:

- + Solution clarity
- + Solubility at various temperatures
- + Viscosity or gel characteristics required
- + Dispersion problems
- + Processing conditions including temperature
- + Rate of hydration
- + Suspension ability
- + Natural versus not natural
- + Particle size desired
- + Ability to stabilize proteins at a low pH
- + Acid stability
- + Availability and cost at the use level required

The gelling agents used in food industry are depicted in Table 2. The concentration of hydrocolloid required to form a gelled product is provided in Table 3.

Table 2. Gelling agents in food industry

Gelling agents	Gel characteristics	Applications
Modified starch	Thermally irreversible opaque gels formed on cooling	Dairy desserts
Agar	Thermoreversible gels on cooling	Bakery products, jellies
k- and i-carrageenan	Thermoreversible gels on cooling	Puddings, milk shakes, tofu
Low methoxyl pectin	Thermoreversible gels on cooling at acidic pH	Jams, jellies, glazes, milk based desserts
High methoxyl pectin	Thermoirreversible gels on cooling at high acidic pH	Jam, jellies
Gellan gum	Thermoreversible highly transparent gels formed on cooling	Water-based fruit flavoured jellies, lemon jelly
Alginate	Thermoirreversible gels do not melt on heating	Restructured foods, cold prepared bakery creams
Methyl and hydroxyl-propylmethyl cellulose	Thermoreversible gels which melt on heating	Salad dressings, cake batters, beverages, whipped toppings

Table 3. Concentration of gelling agent required to form a gel in food product

Hydrocolloid	Concentration of gelling agent, % w/w
Agar	1-2
Alginate	1-2
Carrageenan	0.5-3.0
High methoxy pectin	2-4
Low methoxy pectin	0.1-4.0
Gelatin	1.0-5.0
Gellan	0.5-1.5

Conclusions

Stabilizers perform multitude of functions in several dairy and food products. More and more new stabilizers are being unearthed and applied in the food industry. A blend of several stabilizers and emulsifiers have given better result than using them singly; several food ingredient companies have come up with such proprietary blends of hydrocolloids to give superior results. Nowadays, their role in replacing the high priced food constituents or in cost cutting is a new arena being explored by the researchers.

