Pectins and Gums

5

Introduction

Pectins and gums are important polysaccharides in foods because of their functional properties. They are widely used as gelling agents, thickeners, and stabilizers. They are constituents of plant tissue and are large, complex molecules whose exact nature is not certain. However, enough is known to understand some of their properties and to make use of their functional properties to produce convenience and special texture foods.

To identify a few, pectic acid is found in overripe fruit. Some recognizable gums are seed gums such as guar gum and locust bean gum, and common seaweed polysaccharides including carrageenan and agar.

Pectic Substances

Pectic substances including protopectin, pectinic acid, and pectic acid are an important constituent of plant tissue and are found mainly in the primary cell wall. They also occur between cell walls, where they act as intercellular cement. Although their exact nature is not clear, they can be considered as linear polymers of D-galacturonic acid joined by α-1,4-glycosidic linkages, as shown in Fig. 5.1. Some of the acid or carboxyl (COOH) groups along the chain are esterified with methanol (CH_3OH) as shown.

Each glycosidic linkage is a ***cross-planar*** bond, because it is formed by reaction of one hydroxyl group located above the plane of the first ring with another hydroxyl group located below the plane of the second ring. The configuration of these bonds causes twisting of the molecule, and the resulting polymer can be likened to a twisted ribbon. Cross-planar bonds are not readily digested in the human digestive tract, and so pectins are classified as soluble fiber.

Pectic substances may be grouped into one of the three categories depending on the number of methyl ester groups attached to the polymer. ***Protopectin*** is found in immature fruits, and is a high-molecular weight methylated galacturonic acid polymer. It is insoluble in water yet can be converted to water-dispersible pectin by heating in boiling water. It cannot form gels.

Pectinic acid is a methylated form of galacturonic acid that is formed by enzymatic hydrolysis of protopectin as a fruit ripens. High-molecular weight pectinic acids are known as pectins. Pectinic acids are dispersible in water and can form gels. ***Pectic acid*** is a shorter-chain derivative of pectinic acid that is formed as fruit overripens. Enzymes, such as polygalacturonase and pectinesterase, cause depolymerization and demethylation of the pectinic acid, respectively. Complete demethylation yields pectic acid, which is incapable of gel formation.

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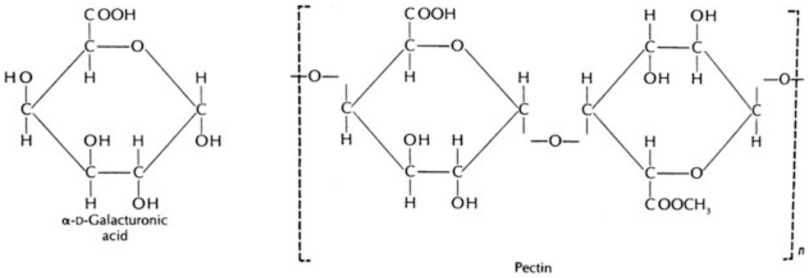
Fig. 5.1 Basic structure of pectic substances



Pectic Substances

Protopectin—methylated galacturonic acid polymer found in immature fruits.

Pectinic acid—methylated galacturonic acid polymer; includes pectins.

Pectic acid—short-chain demethylated derivative of pectinic acid found in over-ripe fruits.

Pectins

Pectins are high-molecular weight pectinic acids and are dispersible in water. Some of the carboxyl groups along the galacturonic acid chain are esterified with methanol. The degree of esterification in unmodified pectins ranges from about 60 % in apple pulp to about 10 % in strawberries. (Pectins can be deliberately deesterified during extraction or processing.) According to the degree of esterification, pectins are classified as *high-methoxyl* or *low-methoxyl* pectins. The two groups have different properties and gel under different conditions.

Low-methoxyl pectins. Low-methoxyl pectins contain mostly free carboxyl groups. In fact, only 20–40 % of the carboxyl groups are esterified. Therefore, most of them are available to form cross-links with divalent ions such as calcium, as shown in Fig. 5.2.

If sufficient cross-links are formed, a three-dimensional network can be obtained that traps liquid, forming a gel. Low-methoxyl pectins can, thus, form gels in the presence of divalent ions without the need for sugar or acid.

High-methoxyl pectins. High-methoxyl pectins contain a high proportion (usually 50–58 %) of esterified carboxyl groups. Most of the acid groups are, therefore, not available to form cross-links with divalent ions, so these pectins do not form gels. However, they can be made to gel with the addition of sugar and acid. It is the high-methoxyl pectins that are commonly used to form pectin jellies.

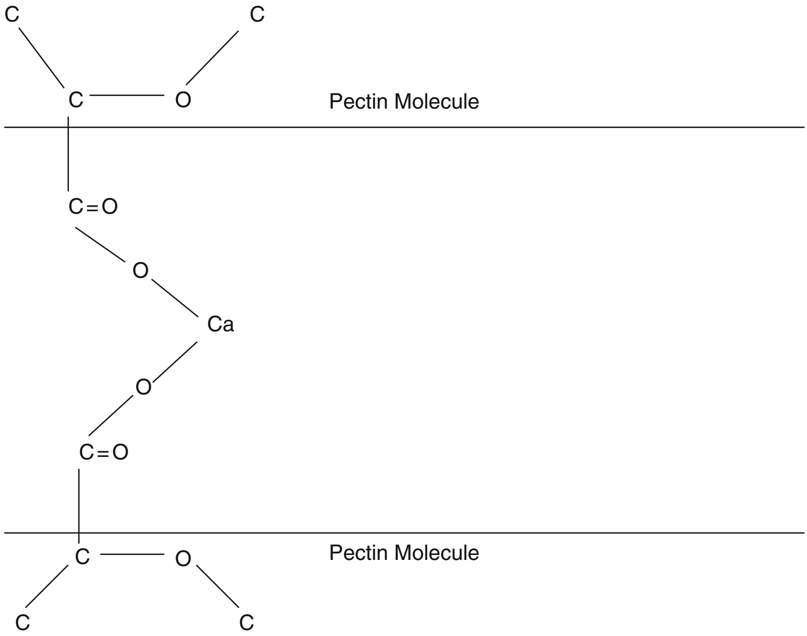
Pectin Gel Formation

A pectin gel consists mainly of water held in a three-dimensional network of pectin molecules. Pectin is dispersible in water and forms a ***sol*** (solid dispersed in liquid continuous phase), although under the right conditions, it can be converted into a ***gel*** (liquid dispersed in solid continuous phase). This occurs when the pectin molecules interact with each other at specific points. It is not easy to form pectin gels; it requires a delicate balance of pectin, water, sugar, and acid.

Pectin is hydrophilic (water loving) due to the large number of polar hydroxyl groups and charged carboxyl groups on the molecule. When pectin is dispersed in *water*, some of the acid groups ionize, and water binds to both the charged and polar groups on the molecules. The negative charge on the pectin molecules, coupled with their attraction for water, keeps them apart so that they form a stable sol.

To form a gel, the forces keeping the pectin molecules apart must be reduced so that they can interact with each other at specific points, trapping water within the resulting three-dimensional network. In other words, the attraction of the pectin molecules for water must be *decreased* and the attraction of the pectin molecules for

Fig. 5.2 Cross-links in low-methoxyl pectin



each other must be *increased*. This can be achieved by addition of sugar and acid.

Sugar competes for water, thus making less water available to associate with the pectin molecules. This reduces the attractive forces between the pectin and water molecules.

Acid adds hydrogen ions, reducing the pH. (The pH must be below 3.5 for a gel to form.) Carboxylic acids contain a ***carboxyl group*** (COOH), are weak acids, and are not fully ionized in solution; the un-ionized form of the acid exists in equilibrium with the ionized form.

$$-\mathrm{COOH} + \mathrm{H_2O} \leftrightharpoons -\mathrm{COO^-} + \mathrm{H_3O^+}$$

When hydrogen ions are added, they react with some of the ionized carboxyl groups to form undissociated acid groups. In other words, the equilibrium is shifted to the left, and more of the carboxylic acid is present in the un-ionized form. Thus, when hydrogen ions are added to pectin, the ionization of the acid groups is depressed and the charge on the pectin molecules is reduced. As a result, the pectin molecules no longer repel each other.

In fact, there is an attractive force between the molecules and they align and interact at specific regions along each polymer chain to form a three-dimensional network. These regions of interaction are called ***junction zones***, shown diagrammatically in Fig. 5.3. However, there are also regions of the pectin chains that are not involved in junction zones because they are unable to interact with each other. These regions form pockets or spaces between the junction zones that are able to entrap water. Hence, a gel is formed, with water trapped in the pockets of the three-dimensional pectin network.

Exactly how the junction zones form is not certain, although hydrogen bonds are thought to play an important role. The ***steric fit*** of the molecules (in other words, their ability to fit together in space) is also important. Pectin molecules contain minor components such as rhamnose and other neutral sugars that are bound to the main galacturonic acid chain by 1-2-glycosidic links. These sugars cause branches or kinks in the molecules and make it difficult for them to align and interact to form junction zones. However, there are regions of the pectin chains that do not contain these neutral sugars and it is

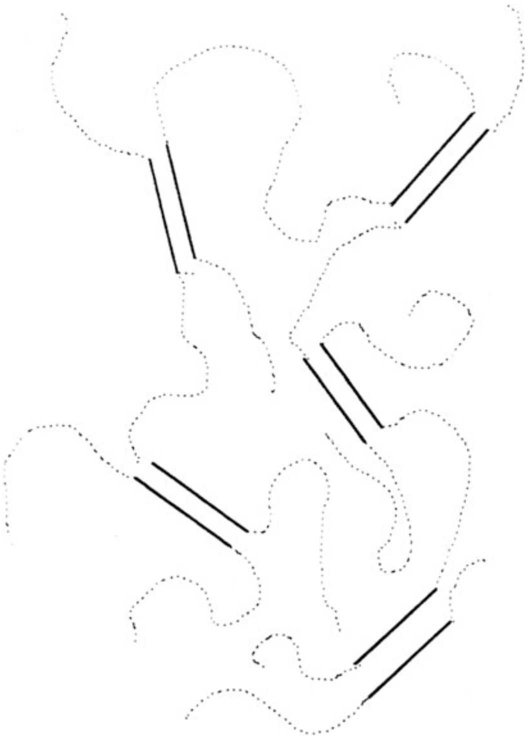


Fig. 5.3 Junction zones in a pectin gel. Generalized two-dimensional view. Regions of the polymer chain involved in junction zones are shown as—. The other regions of the chain are shown as—. Water is entrapped in the spaces between the chains. Adapted from Coultate (2009)

these regions that are thought to form the junction zones.

High-methoxyl pectins form gels in this way. Low-methoxyl pectins require divalent ions to gel, and intermediate pectins require sugar, acid, and divalent ions to gel.

Pectin Sources

Pectins with a high-molecular weight and a high proportion of methyl ester groups have the best jelly-forming ability. The pectin content of fruits is variable and depends not only on the type of fruit but also on its maturity or ripeness. If jellies or jams are made at home, it is best to add commercial pectin to ensure that there is sufficient pectin to form a gel. Purified pectin is made from apple cores and skins (apple pomace) and from the white inner skin (albedo) of citrus fruits. It is available in either liquid or granular form. The granular products have a longer shelf life than the liquids. Low-methoxyl pectin can be obtained by demethylating pectin with enzymes, acid, or alkali until it is 20–40 % esterified (Glicksman 1982). Since these pectins gel with divalent ions and need no sugar, they can be used commercially for the production of low-calorie jams, jellies, or desserts. They have also been introduced to the retail market so that such low-calorie products may be made at home.

Pectin Gel Formation

In a pectin ***sol***

- **Water** binds to ionic and polar groups on pectin.
- **Pectin** molecules are negatively charged and hydrated; therefore, they do not interact with each other.

To form a pectin ***gel***

- Attraction of pectin molecules for water must be decreased.
- Attraction of pectin molecules for each other must be increased.

This is achieved with

- **Sugar**
  - Competes for water.
  - Decreases pectin–water attraction.
- **Acid**
  - Adds hydrogen ions.
  - Depresses ionization of pectin.
  - Reduces the charge on the pectin molecules.
  - Increases pectin–pectin attraction.
- **Pectin**
  - Interacts at junction zones forming a three-dimensional network.
  - Pectin becomes the continuous phase.
- **Water**
  - Is trapped in pockets within the gel network.
  - Water becomes the disperse phase.

Some Principles of Making Jelly

This book does not attempt to describe the practical aspect of making jellies. For such information, the reader is referred to consumer information publications, or to books by authors such as Charley (Charley and Weaver 1998) or Penfield and Campbell (Coultate 2009). The intention is to highlight some of the more important scientific principles of jelly-making.

To make jelly, fruit juice (which is a source of water and acid), pectin, and sucrose are combined in a suitable pan and heated until the mixture boils. The temperature and boiling time are monitored, and boiling is continued until the desired temperature is reached.

As boiling continues, water evaporates, the concentration of sucrose increases, and the boiling point of the jelly also increases. Therefore, the boiling point can be used as an index of sucrose concentration. By measuring the temperature of the boiling jelly, it can be determined when sufficient water has been removed to give the desired sucrose concentration in the final jelly.

However, all solutes increase the boiling point of water, so it is important to allow for the effect of any additional ingredients on the boiling point; a pure sucrose solution may boil at a lower temperature than a jelly mix containing the same concentration of sucrose. In other words, a boiling jelly may contain less sucrose than expected if the effects of the additional ingredients on the boiling point are not taken into account. This could result in a runny or weak gel.

It is important to control the boiling time, not just the temperature of the boiling jelly, because chemical reactions occur in the presence of heat and acid that need to be controlled to maintain gel quality. Glycosidic links are hydrolyzed in the presence of heat and acid. Therefore, depolymerization of pectin will occur if the boiling time is too long. This will result in loss of gelling power and the gel may not set.

During the boiling process, sucrose is converted to invert sugar, and the presence of invert sugar in the jelly prevents crystallization of sucrose on storage over a long period. A short boiling time may not allow formation of sufficient invert sugar to inhibit sucrose crystallization over time, especially if the jelly is stored at refrigeration temperatures.

Boiling Time

- If too long—depolymerization of pectin occurs, and the gel may not set.
- If too short—insufficient invert sugar may be formed, and crystallization of sucrose may occur.

It has already been mentioned that a commercial pectin should be used in addition to the fruit, because the quality of pectin in the fruit varies. An overripe fruit is deficient in pectin, because demethylation and depolymerization occur as the fruit ages. Hydrolysis of only a few glycosidic bonds causes a marked drop in viscosity and gelling power and will produce a weak gel.

Gums

Gums are a group of complex hydrophilic carbohydrates containing thousands of monosaccharide units. Galactose is the most common monosaccharide found in gums; glucose is usually absent. Gums are often referred to as ***hydrocolloids***, because of their affinity for water and their size; when added to water, they form stable aqueous colloidal dispersions or sols. The molecules are highly branched, and as a result most gums are unable to form gels. However, they are able to trap or bind large amounts of water within their branches. Aqueous dispersions therefore tend to be very viscous, because it is difficult for the molecules to move around freely without becoming entangled with each other.

Main Characteristics of Gums

- Larger highly branched hydrophilic polymers
- Rich in galactose
- Hydrocolloids
- Form viscous solutions
- Most do not gel if used alone
- Seaweed polysaccharides form gels

Gums are classified as soluble fiber because they undergo little digestion and absorption in the body. Therefore, they supply relatively few calories to the diet, as compared with digestible carbohydrates such as starch.

Gums are common in a wide range of food products, including salad dressings, sauces, soups, yogurt, canned evaporated milk, ice cream and other dairy products, baked goods, meat products, and fried foods. They are used as thickening agents in food products, replacing starch. They are also used to assist in the stabilization of emulsions and to maintain the smooth texture of ice cream and other frozen desserts. They are common in reduced fat products, because they are able to increase viscosity and help to replace the texture and mouthfeel that was contributed by the fat.

Gums are obtained from plants, and can be separated into five categories: seed gums, plant exudates, microbial exudates, seaweed extracts, and synthetic gums derived from cellulose.

Seed Gums

The seed gums include guar and locust bean gums. These gums are branched polymers containing only mannose and galactose. Guar gum contains a mannose/galactose ratio of 2:1, whereas the ratio is 4:1 in locust bean gum. Guar gum is soluble in cold water, whereas locust bean gum must be dispersed in hot water. Neither gum forms a gel when used alone. However, they may be used synergistically with other gums to form gels.

Guar gum forms gels with carrageenan and guar gum. It is used to stabilize ice cream, and it is also found in sauces, soups, and salad dressings.

The presence of guar gum in the intestine seems to retard the digestion and absorption of carbohydrates and slow absorption of glucose into the bloodstream. Use of guar gum in foods may, therefore, be useful in treating mild cases of diabetes (Penfield and Campbell 1990).

Locust bean gum is typically used as a stabilizer in dairy and processed meat products. It may also be used synergistically with xanthan gum to form gels.

Plant Exudates

The plant exudates include gum arabic, which comes from the acacia tree, and gum tragacanth. These are complex, highly branched polysaccharides. Gum arabic is highly soluble in cold water, and is used to stabilize emulsions and to control crystal size in ices and glazes. Gum tragacanth forms very viscous sols, and is used to impart a creamy texture to food products. It is also used to suspend particles, and acts as a stabilizer in products such as salad dressings, ice cream, and confections.

Categories of Gums

- **Seed gums:** guar gum, locust bean gum
- **Plant exudates:** gum arabic, gum tragacanth
- **Microbial exudates:** xanthan, gellan, dextran
- **Seaweed polysaccharides:** alginates, carrageenan, agar
- **Synthetic gums:** microcrystalline cellulose, carboxymethyl cellulose, methyl cellulose

Microbial Exudates

Xanthan gum, gellan gum, dextran, and curdlan are all gums produced using fermentation by microorganisms. Of these, *xanthan* is the most common. Xanthan forms viscous sols that are stable over a wide range of pH and temperature. It does not form a gel, except when used in combination with locust bean gum. It is used in a wide range of products as a thickener and stabilizer and suspending agent. For example, most salad dressings contain xanthan gum. Xanthan gum is extremely versatile and relatively inexpensive, which makes its presence almost ubiquitous in thickened food products.

Seaweed Polysaccharides

The ***seaweed polysaccharides*** include the agars, alginates, and carrageenans. Unlike most other gums, they are able to form gels under certain conditions.

Carrageenan is obtained from red seaweeds, and especially from Irish moss. It occurs as three main fractions, known as kappa-, iota-, and lambda-carrageenan. Each is a galactose polymer containing varying amounts of negatively charged sulfate esters. Kappa-carrageenan contains the smallest number of sulfate esters, and is therefore the least negatively charged. It is able to form strong gels with potassium ions. Lambda-carrageenan contains the largest number of sulfate groups, and is too highly charged to form a gel. Iota-carrageenan forms gels with calcium ions.

The carrageenan fractions are generally used in combination. Several different formulations are available, containing different amounts of the individual fractions, and food processors are able to choose formulations that best fit their needs.

The carrageenans are used to stabilize milk products such as ice cream, processed cheese, canned evaporated milk, and chocolate milk, because of their ability to interact with proteins. The carrageenans may also be used with other gums, because of their ability to cross-link with them (see more in Food Additives chapter).

Agar is also obtained from red seaweeds. It is noted for its strong, transparent, heat-reversible gels; that is, agar gels melt on heating and re-form when cooled again. Agar contains two fractions—agarose and agaropectin, both of which are polymers of β-ᴅ- and α-ʟ-galactose. Agaropectin also contains sulfate esters.

The **alginates** are obtained from brown seaweeds. They contain mainly ᴅ-mannuronic acid and ʟ-guluronic acid, and they form gels in the presence of calcium ions. Calcium alginate gels do not melt below the boiling point of water; thus, they can be used to make specialized food products. Fruit purees can be mixed with sodium alginate and then treated with a calcium-containing solution to make reconstituted fruit. For example, if large drops of cherry/alginate puree are added to a calcium solution, convincing synthetic cherries are formed. Reconstituted apple and apricot pieces for pie fillings can also be made by rapidly mixing the sodium alginate/fruit puree with a calcium solution and molding the gel into suitable shapes.

Functional Roles of Gums

Gums may be used to perform one or more of the roles in food peoducts.

- **Thickeners**—salad dressings, sauces, soups, beverages
- **Stabilizers**—ice creams, icings, emulsified products
- **Control crystal size**—candies
- **Suspending agents**—salad dressings
- **Gelling agents**—fruit pieces, cheese analogs, vegan jellies
- **Coating agents**—batters for deep-fried foods
- **Fat replacers**—low-fat salad dressings, ice creams, desserts
- **Starch replacers**—baked goods, soups, sauces
- **Bulking agents**—low-fat foods
- **Source of fiber**—beverages, soups, baked goods

CULINARY ALERT! Vegan jellies can be made using products that contain agar, carrageenan, and/or other gums such as locust bean gum and xanthan gum in place of gelatin.

(One such product is *Lieber's Unflavored Jel*, which contains both carrageenan and locust bean gum, and is available from http://www.VeganEssentials.com.)

Synthetic Gums

Cellulose is an essential component of all plant cell walls. It is insoluble in water and cannot be digested by man, and so it is not a source of energy for the body. It is classified as insoluble fiber.

The polymer contains at least 3,000 glucose molecules joined by β-1,4-glycosidic linkages. Long cellulose chains may be held together in bundles forming fibers, as in the stringy parts of celery.

Synthetic derivatives of cellulose are used in foods as *nonmetabolizable* bulking agents, binders, and thickeners. *Microcrystalline cellulose*, known commercially as Avicel (FMC Corp.), is used as a bulking agent in low-calorie foods. It is produced by hydrolysis of cellulose with acid. ***Carboxymethyl cellulose*** (CMC) and *methyl cellulose* (MC) are alkali-modified forms of cellulose. The former is the most common, and it is often called simply *cellulose gum*. It functions mainly to increase the viscosity of foods. It is used as a binder and thickener in pie fillings and puddings; it also retards ice crystal growth in ice cream and the growth of sugar crystals in confections and syrups.

In dietetic foods, it can be used to provide the bulk, body, and mouthfeel that would normally be supplied by sucrose. *Methyl cellulose* forms gels when cold dispersions are heated. It is used to coat foods prior to deep fat frying, in order to limit absorption of fat. Two other forms of modified cellulose include *hydroxypropyl cellulose* and *hydroxypropylmethyl cellulose*. These are also used as batters for coating fried foods.

As well, there may be a synergistic effect of using various gums together. This is most likely the case when more than one gum name appears on a food label!

Conclusion

Pectins and seaweed polysaccharides are useful for various food products because of their gelling ability. In general, gums are important because they form very viscous solutions, but most do not gel. All these carbohydrates are important to the food industry because of their functional properties and their ability to produce foods with special textures. Used in a wide range of food products, as gelling agents, thickeners, and stabilizers, their availability has increased the choice and quality of many convenience foods. Synthetic derivatives of cellulose are important as nonmetabolizable bulking agents, thickeners, and stabilizers in a wide range of calorie-reduced foods.

Notes

CULINARY ALERT!

Glossary

Carboxyl group COOH group; weak acid group that is partially ionized in solution.

Carboxymethyl cellulose (CMC) Synthetic derivative of cellulose used as a bulking agent in foods. Also known as cellulose gum.

Cellulose Glucose polymer joined by β-1,4-glycosidic linkages; cannot be digested by humans, and so provides dietary fiber.

Cross-planar bond Formed when the hydroxyl groups on the carbon atoms involved in the formation of a glycosidic bond are oriented on opposite faces of the sugar rings. Cross-planar bonds occur in pectin and cellulose. They are not digested in the human digestive system.

Gel Two-phase system with a solid continuous phase and a liquid dispersed phase.

Gums Complex, hydrophilic carbohydrates that are highly branched and form very viscous solutions; most gums do not gel.

High-methoxyl pectin Pectin with 50–58 % of the carboxyl groups esterified with methanol.

Hydrocolloid Large molecule with a high affinity for water that forms a stable aqueous colloidal dispersion or sol. Starches, pectins, and gums are all hydrocolloids.

Junction zone Specific region where two molecules such as pectin align and interact, probably by hydrogen bonds; important in gel formation.

Low-methoxyl pectin Pectin with 20–40 % of the carboxyl groups esterified with methanol.

Pectic acid Shorter-chain derivative of pectinic acid found in overripe fruits; demethylated; incapable of forming a gel.

Pectic substances Include protopectin, pectinic acids, and pectic acids.

Pectin High-molecular-weight pectinic acid; methylated α-D-galacturonic acid polymer.

Pectinic acid Methylated α-D-galacturonic acid polymer; includes pectins; can form a gel.

Protopectin Insoluble material found in immature fruits; high-molecular weight methylated galacturonic acid polymer; cannot form a gel.

Seaweed polysaccharides Complex polysaccharides that are capable of forming gels; examples include alginates, carrageenan, and agar; used as thickeners and stabilizers in food.

Sol or dispersion Two-phase system with a solid dispersed phase and a liquid continuous phase.

Steric fit Ability of molecules to come close enough to each other in space to interact (or fit together).

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