Consortium for
Educational
Communication

Module on

POLYSACCHARIDES AND THEIR SIGNIFICANCE

By

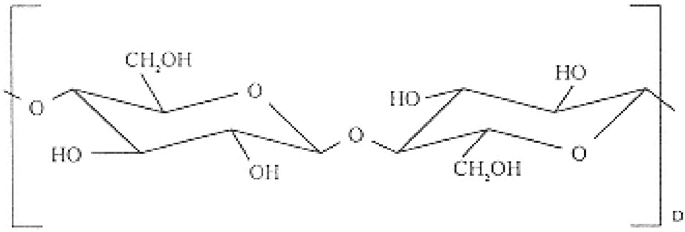
ASMA ASHRAF KHAN
Research Scholar
Department of Food Technology,
UNIVERSITY OF KASHMIR,
Srinagar- 1900 06

Introduction

Polysaccharides are ubiquitous biopolymers built up from few types of hexoses, hexose derivatives (uronic acid and sulphate derivatives) and pentoses. They are high molecular weight substances composed of a large number of monosaccharide units to form one large molecule. Polysaccharides commonly found in food are starch, dextrins, glycogen, cellulose, hemicelluloses, pentosans and pectic substances. The general scientific term for polysaccharides is ***glycans***. Polysaccharides which consist of one type of sugar structural units are homoglycans, and if two or several types of sugar units, they are heteroglycans. The monosaccharides may be joined in a linear pattern (as in cellulose and amylose) or in a branched fashion (amylopectin, glycogen, guaran). The number of monosaccharide units in a polysaccharide, termed its degree of polymerization (DP), varies. Only a few polysaccharides have a DP less than 100; most have DPs in the range 200–3000. Their acidic hydrolysis yields monosaccharides. Partial chemical and enzymatic hydrolysis, in addition to total hydrolysis, are of importance for structural elucidation. The larger ones, like cellulose have a DP of 7000–15,000. The frequency of branching sites and the length of side chains can vary greatly (glycogen,guaran). It is estimated that more than 90% of the considerable carbohydrate mass in nature is in the form of polysaccharides and 99% are in plants. Polysaccharides are extremely common in nature and cellulose is the most common organic compound on the planet. Polysaccharides serve plants and animals in three ways: cellulose, hemicelluloses, pentosans and pectic substances provide structural material (cell walls, fibres, seed coats, peel and husks).chitin and mucopolysaccharides (polysaccharides containing amino acids) serve this purpose in animals. Starch, dextrin and fructan in plants, and glycogen in animals, provide food reserves polysaccharides attract and retain water so that lifes enzymic processes are not impeded under dehydrating conditions. Isolated polysaccharides are utilized to a great extent in food processing ,either in native or in modified forms, as: thickening or gel-setting agents (starch, alginates, pectin, guaran gum);stabilizers for emulsion and dispersions; film forming, coating substances to protect sensitive food from undesired changes and inert fillers to increase the proportion of indigestible ballast substances in a diet.

CELLULOSE

Cellulose is the world’s most abundant naturally occurring organic substance, rivaled only by chitin. It has been estimated that nature synthesizes from 100 to 1000 billion (10^{11} to 10^{12}) metric tons of cellulose every year. It is therefore not surprising that humans have made use of cellulose on a vast scale in the paper, mining, building and allied industries, and as a source of bioenergy. Wood pulp is the main source of processed cellulose, the bulk of which is converted to paper and cardboard, and about 2%, amounting to just over 3 million tons, into regenerated fiber and films or chemical derivatives. Cellulose is a high-molecular-weight, linear, insoluble homopolymer of repeating β-D-glucopyranosyl units joined by (1 -4) glycosidic linkages. Because of their linearity and stereoregular nature, cellulose molecules associate over extended regions, forming polycrystalline, fibrous bundles. Crystalline regions are held together by large numbers of hydrogen bonds. They are separated by, and connected to, amorphous regions. Cellulose is insoluble because, in order for it to dissolve, most of these hydrogen bonds would have to be released at once. Cellulose can, however, through substitution, be converted into water-soluble gums. Cellulose and its modified forms serve as dietary fiber because they do not contribute significant nourishment or calories as they pass through the human digestive system. A purified cellulose powder is available as a food ingredient. High-quality cellulose can be obtained from wood through pulping and subsequent purification. Chemical purity is not required for food use because cellulosic cell-wall materials are components of all fruits and vegetables and many of their products. The powdered cellulose used in foods has negligible flavor, color, and microbial contamination. Powdered cellulose is most often added to bread to provide non caloric bulk. Reduced-calorie baked goods made with powdered cellulose, not only have an increased content of dietary fiber, but also stay moist and fresh longer.



Cellulose (repeating units)

One of the certainties in cellulose science is that cellulose is an aggregate of linear polymers of D-glucopyranosyl residues in the chain form, which are linked together entirely in the β-1,4 configuration. Cellulose is a hygroscopic material, insoluble but able to swell in water, dilute acid, and most solvents. Solubility can be achieved in concentrated acid but at the expense of considerable degradation through acetal (glycosidic) hydrolysis. Alkali solutions lead to considerable swelling and dissolution of hemicelluloses present. Cellulose is not digested in the human system and acts as roughage or dietary fibre, It can be broken down to glucose by certain microbial enzymes. This is the way cellulose is hydrolyzed in the rumen of animals to provide them with sugar. Some physically modified celluloses are used in food processing units like:

Microfibrillated Cellulose

The assay for microfibrillated cellulose (MFC) is described in the Food Chemicals Codex (FCC) and involves titration by ferrous ammonium sulfate of a potassium dichromate and sulfuric acid-treated solution of the cellulose. The assay specifies at least 97% cellulose. MFC has considerably more water-retention capability than normal-grade materials and is considerably less prone to precipitation in the cupriethylenediamine residue test (cuene test)

Microcrystalline Cellulose

Microcrystalline cellulose (MCC) is produced by treating natural cellulose with hydrochloric acid to dissolve the amorphous regions of the polysaccharide, leaving behind the less reactive crystalline regions as fine crystals. As with MFC, the viscosity of dispersions of this product is both pH and heat invariant. A number of varieties are available — powdered, bulk-dried colloidal, spray-dried colloidal (with CMC), and spray-dried with sweet whey. MCC dispersions have been shown to exhibit both thixotropic and pseudoplastic behavior.

Chemically modified cellulose derivatives

Despite the wide variety of cellulose derivatives that have been made, notably acetate and nitrate esters, only a few of the cellulose ethers find application (and are approved for use) in foodstuffs. The most widely used cellulose derivative is sodium CMC; other ethers have unique and interesting properties, however, which ensure their inclusion in a widening array of products. Thus, for example, Methyl cellulose (MC) and hydroxyl propyl methyl cellulose (HPMC) find uses as a result of interfacial activity and their ability to form gels on heating. Although a number of cellulose ethers are available, they are all made in essentially the same manner. Naturally, individual suppliers have their own technologies, but the production process can be broken down into the generation of alkali cellulose, alkylation or hydroxyalkylation, and finally product purification. Alkylation specifically at primary alcohol sites requires a more elaborate synthetic procedure.

Applications in food:

Cellulose and its physical and chemical derivatives have long been used in fabricating formulated foods. The physically modified celluloses are useful in many products where bulk properties are desirable. This would include reduced- or low-calorie foods, flavor oil imbibers, or flowable products such as artificial sweeteners and flavor packets. The use of these cellulosics is generally due to their rheology, controlled water interaction, and textural attributes, and not to solubility or other chemical properties. Hence, MCC and finely ground cellulose perform a valuable bulking role in low-calorie foods. Five important roles for the chemically modified cellulose derivatives in foods are the regulation of rheological properties, emulsification, stabilization of foams, modification of ice crystal formation and growth, and water-binding capacity. The applicability of cellulose derivatives for specific food applications can be determined from their physical and chemical properties. When a choice is to be made, a number of parameters must be considered: (a) the chemical structure of the polymer; (b) the molecular weight of the polymer; (c) the presence of other active ingredients in the food matrix; (d) the processing operations to which the food will be subjected; and (e) the physical properties, including fiber dimension of the polymer.

STARCH

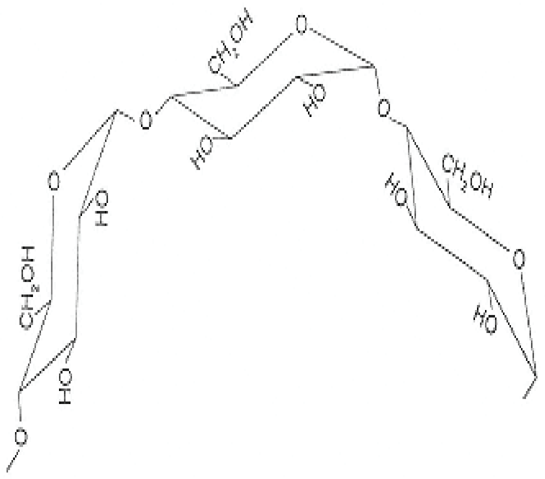
Starch unique chemical and physical characteristics and nutritional quality set it apart from all other carbohydrates. Starch is the predominant food reserve substance in plants and provides 70–80% of the calories consumed by humans worldwide. Starch and starch hydrolysis products constitute most of the digestible carbohydrate in the human diet. Starch is unique among carbohydrates because it occurs naturally as directly particules (granules). Starch granules are relatively dense and insoluble and hydrate only slightly in cold water. They can be dispersed in water, producing low-viscosity slurries that can be easily mixed and pumped, even at concentrations of greater than 35%. The viscosity-building (thickening) power of starch is realized only when a slurry of granules is cooked. Commercial starches are obtained from cereal grain seeds, particularly from corn, waxy corn (waxy maize), high-amylose corn, wheat, and various rices, and from tubers and roots, particularly potato, sweet potato, and tapioca (cassava). Starches and modified starches have an enormous number of food uses, including adhesive, binding, clouding, dusting, film forming, foam strengthening, antistaling, gelling, glazing, moisture retaining stabilizing, texturizing, and thickening applications. A second uniqueness is that most starch granules are composed of a mixture of two polymers: an essentially linear polysaccharide called amylose, and a highly branched polysaccharide called amylopectin.

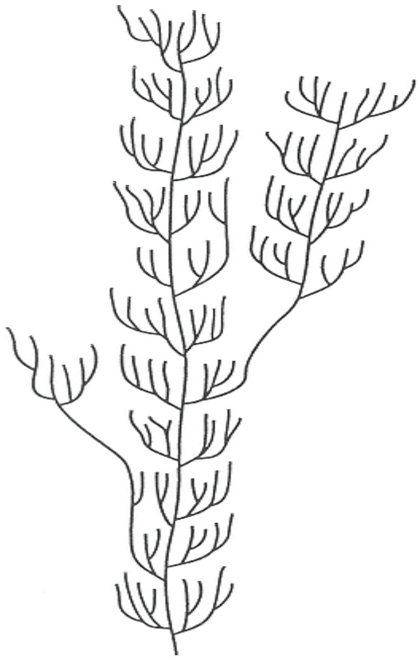
Amylose

Amylose is essentially a linear chain of (1-4)-linked α-D-glucopyranosyl units is in glycosidic linkage with carbon atom 4 of the next glucose unit. Amylose molecules have molecular weights of about 10^6.amylose is not truely soluble in water but forms hydrated micelles. In such micelles the long chain is twisted into a helical coil .The two so-called high-amylose corn starches that are commercially available have apparent amylose contents of about 52% and 70–75%.

Amylopectin

Amylopectin is a very large, very highly branched molecule, with branch-point of α-(1-4) linkages, but in addition, the molecule is branched through α-(1-6)linkages to the extent of 4-5percent. Molecular weights of from 10^7 to 5×10^8 make amylopectin molecules among the largest. Amylopectin is present in all starches, constituting about 75% of most common starches .Some starches consist entirely of amylopectin and are called waxy starches. Waxy corn (waxy maize), the first grain recognized as one in which the starch consists only of amylopectin, is so termed because when the kernel is cut the new surface appears vitreous or waxy. Other all-amylopectin starches are also called waxy although, as in corn, there is no wax content. Potato amylopectin is unique in having phosphate ester groups, attached most often (60%-70%) at an O-6 position, with the other third at O-3 positions.





a)A trisaccharide segment of an unbranched b)
A diagrametic representation of a portion of an amylopectin

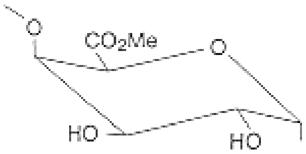
portion of amylose or amylopectin molecule.

Uses of starch in food technology:

Cereal kernels may be flaked, rolled, or puffed to make ready-toeat (RTE) products, or they may be milled into flours (containing about 75% of starch), which represent an enormous volume usage in breads, pizzas, and other baked products. Disruption of the granule is generally the first step in converting native starch into useful products, and practically all of the hundreds of starches that are marketed as such are thus modified or derivatized in some way. The use of modified starches is generally controlled by government regulation, a complex issue in view of the growing emphasis on fat replacers, products less nutritive but with similar taste and mouth feel to the genuine article; small starch granules can serve the same purpose, replacing up to 50% of the fat in frozen desserts. Novel pharmaceutical properties of starch derivatives are exemplified by the 3,5-dinitrobenzoate, which finds application in cases of renal failure on account of its ability to sequester creatinine.

Pectins

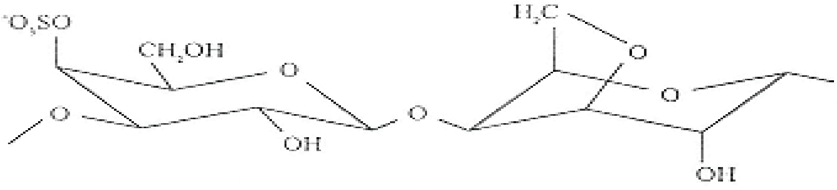
The term pectins usually used in a generic sense to designate those water-soluble galacturonoglycan preparations of varying methyl ester contents and degrees of neutralization that are capable of forming gels. In all natural pectins, some of the carboxyl groups are in the methyl ester form. Commercial pectins are galacturonoglycans [poly(β-D-galactopyranosyluronic acids) with various contents of methyl ester groups. Native pectins found in the cell walls and intercellular layers of all land plants are more complex molecules that are converted into commercial products during extraction with acid. Commercial pectin is obtained from citrus peel and apple pomace. Pectin from lemon and lime peel is the easiest to isolate and is of the highest quality. Pectins have an unique ability to form spreadable gels in the presence of sugar and acid or in the presence of calcium ions and are used almost exclusively in these types of applications. The compositions and properties of pectins vary with source, the processes used during preparation, and subsequent treatments. During extraction with mild acid, some hydrolytic depolymerization and hydrolysis of methyl ester groups occurs. Depending on the isolation conditions, the remaining free carboxylic acid groups may be partly or fully neutralized, that is, partly or fully present as sodium, potassium, or ammonium carboxylate groups. Typically, they are present in the sodium salt form. LM pectin, since it does not require sugar for gelation, is used to make dietetic jams, jellies, and marmalades.



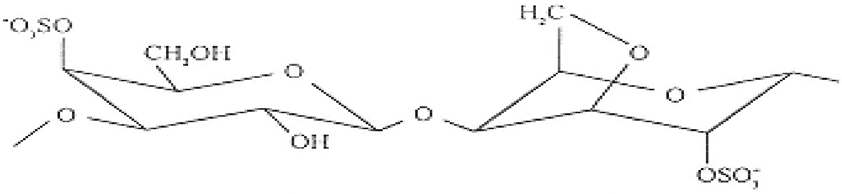
The most prevalent monomeric unit of a hig h-methoxyl pectin.

Carrageenans

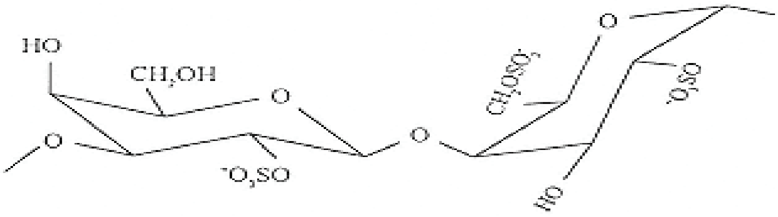
The carrageenans are mixtures of several related galactans having sulfate half-ester groups attached to the sugar units. They are extracted from red seaweeds with a dilute alkaline solution; the sodium salt of a carrageenan is normally produced. Carrageenans are linear chains of D-galactopyranosyl units joined with alternating (1 3)-β-D- and (1 4)-β-D-glycosidic linkages, with most sugar units having one or two sulfate groups esterified to a hydroxyl group at carbon atoms C-2 or C-6. This gives a sulfate content ranging from 15 to 40%. Units often contain a 3,6-anhydro ring. The principal structures are termed kappa (k), iota, (ı), and lambda (λ) . There are both gel forming and non gel forming carrageenan fractions. Both form stable complexes with proteins and other gums. They are used in dairy products because they form stabilizing complexes with milk proteins to give a more acceptable texture to processed dairy products. Carrageenan products, of which there may be well more than 100 for different specific applications from a single supplier, contain different proportions of the three main behavioral types: kappa, iota, and lambda.



κ-Carrageenan



ι-Carrageenan



λ–Carrageenan

Idealized unit structures of kappa-, iota-, and lambda-type carrageenans.

Glycogen

This is a storage polysaccharide in animals, and hence is sometimes called animal starch. Glycogen is made primarily by the liver and the muscles, but can also be made by glycogenesis within the brain and stomach.Liver glycogen rapidly hydrolyzes to D-glucose after slaughter of animals. Glycogen is a branched-chain polysaccharide resembling amylopectin rather than amylose, but is more branched than amylopectin. In the liver hepatocytes, glycogen can compose up to eight percent (100–120 g in an adult) of the fresh weight soon after a meal. Only the glycogen stored in the liver can be made accessible to other organs. In the muscles, glycogen is found in a low concentration of one to two percent of the muscle mass. The amount of glycogen stored in the body—especially within the muscles, liver, and red blood cells varies with physical activity, basal metabolic rate, and eating habits such as intermittent fasting. Small amounts of glycogen are found in the kidneys, and even smaller amounts in certain glial cells in the brain and white blood cells. The uterus also stores glycogen during pregnancy, to nourish the embryo. Glycogen is composed of a branched chain of glucose residues. It is stored in liver and muscles. It is insoluble in water. It turns red when mixed with iodine. It also yields glucose on hydrolysis.

Chitin

Chitin is one of many naturally occurring polymers. It forms a structural component of many animals, such as exoskeletons. Over time it is bio-degradable in the natural environment. Its breakdown may be catalyzed by enzymes called chitinases, secreted by microorganisms such as bacteria and fungi, and produced by some plants. Some of these microorganisms have receptors to simple sugars from the decomposition of chitin. If chitin is detected, they then produce enzymes to digest it by cleaving the glycosidic bonds in order to convert it to simple sugars and ammonia. Chemically, chitin is closely related to chitosan (a more water-soluble derivative of chitin). It is also closely related to cellulose in that it is a long unbranched chain of glucose derivatives. Both materials contribute structure and strength, protecting the organism.

Gums

These are hydrophilic substances that give a viscous solution or dispersions when treated with hot or cold water. Most gums are polysaccharides these are incorporated to improve texture, water retention and rehydration of many dehydrated ,frozen and instant convenient foods. Gums function as thickners for gravies and sauces, emulsion stabilizers in salad dressings, foam stabilizers in whipped popping and beer, clarifying agents for wines & beer, flavor fixing agents & lubricants. The best known plant exudates are gum Arabic (Acacia), karaya & tragacanth.

Agar: It is an extract from red and brown algae. It is mainly β-D and α-L-galactan where galactose residues are sulphated at various hydroxyl positions. Agar forms the strongest and most stable gels at lowest concentrations. Agar gels are transparent and reversible upon heating and cooling. Therefore, agar finds several uses in stabilizing food products.

Curdlan: Curdlan is a bacterial polysaccharide produced by *Agrobacterium biovar.* It is a 1,3-linked β-glucan that has the unique property of forming gels when solutions of it are heated. Curdlan forms two types of gels that differ in thermoreversibility. A thermally reversible gel is formed when solutions of Curdlan are heated to about 65^{o}C,then cooled to about 60^{0}C.However,when Curdlan solutions are heated to about 80^{0}C, a strong thermally irreversible gel forms, that is ,a solution is not reformed upon cooling. Gel strength continues to increase with increasing temperature upto about 130^{0}C.

Algin: It is a product of brown algae. It is composed of D-mannuronic and D-galacturonic acid .The carboxylic groups are neutralized by various natural cations. If they are replaced by a single cation (sodium, potassium, ammonium,etc) the product is called an alginate. When the cations are removed insoluble alginic acid are produced. Alginates give widely variable sols and viscosity properties in acid and salt solutions. They form gels and films and find a number of food uses.

Dietary fibre:

Dietary fibre is defined as the edible parts of plants or analogous carbohydrates that are resistant to digestion and absorption in the human small intestine. Dietary fiber is often divided into soluble and insoluble fiber. Gum, mucilages, and pectin are soluble fibers where as cellulose, lignin, and hemi- cellulose is insoluble fiber. One of the important dietary fiber is β-glucan. It is a linear chain of β-D-glucopyranosyl units. About 70% are linked (1 -4) and about 30% (1 -3). Such (1-4, 1-3)-β-glucans are often called mixed-linkage β-glucans. When taken orally in foods, β-glucans reduce postprandial serum glucose levels and the insulin response—that is, they moderate the glycemic response—in both normal and diabetic human subjects. They also decrease blood cholesterol levels, lessening the chance of heart disease and reduces the chances of colonic cancer, probably due to their sweeping action. They increase intestinal and fecal bulk, which lowers intestinal transit time and helps prevent constipation. Their presence in foods induces satiety at meal time. Nutritionists set requirements of dietary fiber at 25–50 g/day. Cereal brans, kidney and navy beans are especially good sources of dietary fiber. A product based on psyllium seed hulls has high water-binding properties, leading to rapid transit time in the gastrointestinal tract, and is used to prevent constipation. Table 1 gives an overview of the uses of polysaccharides in food technology.

Table 1.

Area of application/food	Suitable polysaccharides
Stabilization of emulsions/ suspensions in condensed milk and chocolate milk	Carrageenan,algin,pectin,carboxymethyl cellulose
Water binding,improvement of consistency, yield increase of soft cheese, cream cheese.	Carrageenan,agar,gum tragacanth, karaya gum,algin,locust bean flour, carboxymethylcellulose
Thickening and gelation of milk in puddings made with or without heating,cream;improvement of consistency	Pectin, algin, carrageenan, guaran gum, locust-bean flour, CMC, modified starches
Jellies for meat, fish, and vegetables	Algin, carrageenan, agar

Prevention of starch retrogradation in bread and cakes, water binding in dough	Agar,guaran gum,locust bean flour,carrageenan,xanthum gum
Thickening and gelation of fruit pulp(confiture,jams,jellies,fruit pulp for icecream and yoghurt)	Pectin ,algin
Gelation of jelly candies,jelly beans,glaze,icing,water-dessert jellies	Pectin , algin, carrageenan, agar, gum arabic, modified starches

Source: Food Chemistry by Belitz.Grosch, 2nd edition springer