

LECTURE 4: Cross-linked and other derivative of starches

A great number of esters and ethers of starch, with an infinite range of physicochemical properties (particularly with regard to the heat stability), can be prepared. But use of such derivatives in food is restricted and only a few of these are important in the food industry. Starch phosphates, which have analogues in the amylopectin fraction of root and tuber starches, are examples of starch derivatives which are suitable as food additives. The introduction of free-acid groups in starch phosphates both increases and stabilizes the paste viscosity by the

- Negatively charged phosphate groups expand the molecule in solution
- Coulombic repulsion
- Prevent the formation of aggregates

Because of their high viscosity and paste clarity, starch phosphates are put to extensive use in foods as thickness and texturizing agents. Their resistance to molecular aggregation is of importance in the formulation of frozen foods. The swelling and ultimate breakdown of starch granules during cooking can be controlled by introducing a suitable number of cross-linkages between the molecules.

Cross linked phosphate esters may be prepared commercially by esterification with trimetaphosphate. The extent of cross linking is measured by the change in the pasting properties of the derivatives. Starch with low level of phosphate cross linking is also used in textural modification of food e.g. Cross bonded phosphate starches are used as thickeners in salad cream and fruit-pie fillings. The introduction of hydroxyalkyl substituent increases the solubility of starch and prevents molecular aggregation e.g. hydroxypropyl starch. Hydroxyalkyl starches gelatinize at lower temperature than the parent starch and paste show little tendency to form gels.

Cellulose

Cellulose is the most abundant polysaccharide in nature, since one-third of all higher plants consists of this biopolymer which functions as the main structural material. It is a linear polymer of D-glucose units linked (1 à 4) in the β - configuration. The cellulose chains are unbranched, and may contain as many as 5000 glucose units. Because of the β -1,4 linkage, the glucose units in the chain alternate, and the molecule is effectively a rigid and straight chain. As a result, cellulose molecules can readily align themselves side-by-side in an arrangement which is stabilized by intermolecular hydrogen bonding and form crystalline regions. Intermolecular bonding is so strong that cellulose is insoluble in water, and even in strong sodium hydroxide solution. The cellulose is responsible for the form and gross texture in all foodstuffs prepared from plants. Being insoluble, it is little affected by any cooking process and does not disperse. On ingestion, it is unaffected by enzymes in the digestive tract and does not hydrate.

Glycogen

Glycogen the reserve carbohydrate is a polysaccharide found in the animal body. It is found mainly in the muscles (0.5 to 1 percent) and liver (3 to 7 percent). Glycogen resembles starch in its chemical properties. It is formed by the condensation of a large number (5000-10000) of glucose molecules. It is a branched chain polysaccharide, resembling amylopectin. The chain length varies from 8 to 12 glucose units. The molecular weight of glycogen from different sources range from 105 to 108 daltons.

Hemicellulose

Hemicelluloses are present in many plant tissues. They are structural components of the cell wall. They are water-insoluble, non-starchy polysaccharides. They are heteropolysaccharides. Monosaccharide units present in hemicelluloses are xylose, arabinose, galactose, glucose, glucuronic acid. Hemicelluloses are nonfibrous while celluloses are fibrous. They are more soluble in alkali and more readily hydrolyzed by dilute acids than celluloses.

Pectin

The pectins or pectic substances are found universally in the primary cell walls & intercellular layers in plants. They are most abundant in young tissue. They are characteristic constituent of fruits e.g. citrus fruits contain 30% pectin. The pectic substances are a family of very closely associated polysaccharides which are very difficult to separate. The term 'pectin' is used in relation to water insoluble substances. D-galacturonic acid is the principal constituent which is esterified as methyl ester and possess considerable gelling power. Other constituents include D-galactose, L-arabinose, D-xylose, L-rhamnose and L-fucose. Three types of homopolysaccharides are also present – D-galacturonan, D-galactan, and L-arabinan. Typical heteropolysaccharides associated with pectic substance include the soyabean L-arabino-D-galactan. Preparations in which more than half of the carboxyl groups are in the methyl ester form are classified as high-methoxyl pectins, the remainder of the carboxyl groups will be present as a mixture of free acid and salt forms. Preparations in which less than half of the carboxyl groups are in the methyl ester form are called as low-methoxyl pectins. Pectin is widely used in marmalade and jelly preparation. High-methoxyl pectin solutions gel sufficient acid and sugar are present. Low-methoxyl pectin solutions gel only in the presence of calcium ions, which provide cross bridges.

Agar

Agar is obtained from the family of red seaweeds (Rhodophyceae). Example of some species are *Gelidium cartilagineum* and *Gracilaria confervoides*. Agar consists of a mixture of agarose and agaropectin. Agarose is a linear polymer. The main components of chain are β -D-galactopyranose and 3,6-anhydro- α -L-galactopyranose, which alternate through 1, 4 and 1, 3 linkages. The chains are esterified to a low extent with sulphuric acid. Agaropectin fraction has a high sulphate esterification degree as compared to agarose fraction. Agarose is the main gelling component of the agar. Agar is insoluble in cold water. It dissolves to give random coils in boiling water. It

forms heat resistant gels. Agar has a major use in preparation of microbiological media. Agar is added to frozen desserts and ice cream as stabilizer.

Alginates

Alginates or Alginic acid is the most common algal polysaccharide, found in brown seaweeds (*Laminaria* spp.). This linear polysaccharide is composed of β -D-mannuronic acid and α -L-guluronic acid, both linked through the (1 \rightarrow 4) positions. These monomer units do not occur randomly but are present in relatively long sequence of each type. It is commonly used as a gelling and stabilizing agent to improve the texture of products such as ice-cream, pie filling and icings. It forms irreversible gels in cold water in presence of calcium ions. It prevents formation of larger ice crystals in ice creams during storage.

Carrageenan

The term carrageenan covers a range of sulphated galactans which are linked alternatively by (1 \rightarrow 3) and (1 \rightarrow 4) glycosidic bonds. The carrageenans can be fractionated into six types which vary depending on the degree and manner of sulphation and the presence or absence of 3,6 – anhydro galactose units. These are lambda, kappa, iota, mu, nu and theta.

The various fractions do not occur together. The most important forms are lambda, kappa and iota. The polysaccharides have high molecular weight in the range of 1,00,000 to 10,00,000. They are regarded as being non-absorbable in the digestive tract of man.

The solubility properties of these polysaccharides depends on the

- (i) Proportion of sulphate groups
- (ii) Cations associated with them
- (iii) Proportion of 3,6-anhydrogalactose residues (relatively hydrophobic)

Lambda fraction is easily soluble in water because of the high proportion of sulphate groups and the absence of anhydrogalactose, and is unaffected by the nature of cations present. Kappa fraction contains a lower proportion of sulphate groups and some anhydrogalactose units, and as a result is only soluble in water in the form of sodium salt. Other cations (K^+ and Ca^{2+}) only allow swelling in cold water, and heating to 60°C is necessary to ensure solubilization. Iota fraction has an intermediate structure and properties.

Because of the presence of the strongly charged anionic sulphate group, the carrageenans as a group are able to form a complex not only with cationic materials but also with amphoteric substance such as proteins. This unique property of carrageenan extracts can be utilized as a stabilizer for condensed milk.

Gums

Gums may be formed spontaneously; or at the site of injury to the plant. They are exuded as viscous fluids which become dehydrated to give hard, clear nodules consisting mainly of polysaccharides. These are known as exudate gums. Many such

gums from tropical countries find uses in the food industry as thickening agents or emulsion stabilizers. e.g. gum arabic, gum tragacanth, gum ghatti, gum karaya etc. These polysaccharides all possess complex highly-branched structure with D-glucuronic and/or D-galacturonic acids, together with two or more neutral sugars. The acidic residues are found naturally as salts and some of the sugars are esterified with acetic acid.

As a group, the gums are probably the most complex of all natural polymers and structural investigations are very difficult. Most likely, a gum is a group of closely related molecular species in which varying side chains are attached to a main backbone. Galactomannan gums such as locust bean gum and guar gum come from seeds produced by leguminous plants of *Cyamopsis* and *Ceratonia* genera. Guar gum is obtained from the ground endosperm of the leguminous plant *Cyamopsis tetragonoloba*. Guar gum consists of a linear chain of β -D-mannose units joined with 1, 4 linkages. Every second residue has a side chain, a galactose unit that is bound to the main chain by a α -1, 6 linkage. Guar gum is nongelling, and is used as a viscosity builder, stabilizer, and water binder. Guar gum is used in ice cream, desserts, salad dressings, bakery products, sauces, soups.

Locust bean gum is present in the endosperm of seeds obtained from the evergreen tree, *Ceratonia siliqua*. Locust bean gum is made up of mannose and galactose. The ratio of mannose to glucose is 4. It is insoluble in cold water. It is compatible with other gums. It readily forms gel when combined with xanthan gum. Functions of locust bean gum include thickening, stabilization of emulsion and inhibition of syneresis. It is used in sauces, beverages, cheese, ice cream.