

FOOD SCIENCE AND TECHNOLOGY

Lecture23

Lecture 23: Starch, Cellulose and Pectin

Hello friends, Namaskar. So, in this next half an hour, in lecture number 23 today, we will talk about starch, cellulose and pectins; mainly the major polysaccharides found in food materials.

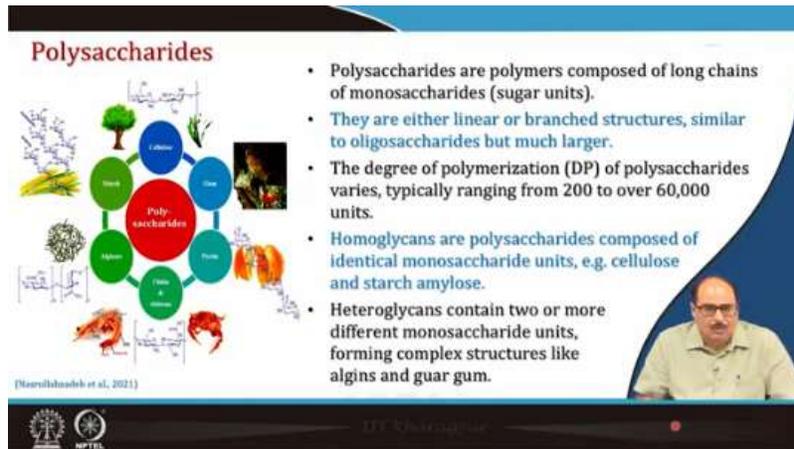


We will discuss the properties of polysaccharides and their classification, and then the important polysaccharides, their functional properties and characteristics, we will discuss.



These polysaccharides include starch, dextrin, and pectic substances. We will also cover some important aspects of cellulose, hemicellulose, glycogen, gums, and mucilages.

Finally, we will discuss major points like gelatinization and retrogradation of starch which are important processes in food processing, particularly grain processing, etc. Then, pectin hydrolysis, which is a major phenomenon, particularly in the case of fruits and vegetables and all those things, which affects their properties and characteristics during processing, handling, and storage.



Polysaccharides

- Polysaccharides are polymers composed of long chains of monosaccharides (sugar units).
- They are either linear or branched structures, similar to oligosaccharides but much larger.
- The degree of polymerization (DP) of polysaccharides varies, typically ranging from 200 to over 60,000 units.
- Homoglycans are polysaccharides composed of identical monosaccharide units, e.g. cellulose and starch amylose.
- Heteroglycans contain two or more different monosaccharide units, forming complex structures like algin and guar gum.

(Nisarullahahab et al, 2021)

So, as you know, in the last class, we discussed monosaccharides and oligosaccharides. When we were discussing oligosaccharides, we discussed that is the monosaccharide unit they join together with the help of glycosidic linkages and their polymers are formed that is the macromolecules are formed particularly when the joining monosaccharide unit in a polymer is less than 10 and when the polysaccharide is a monomer unit or monosaccharide units are more than 10, then the resulting macromolecule is called as a polysaccharide. So basically, these are polymers, and polysaccharides are polymers composed of long chains of monosaccharides or sugar units. They are either linear or branched structures, and they are almost similar to oligosaccharides, but they are much much larger than the oligosaccharides. The degree of polymerization of polysaccharides varies Typically ranging from 200 to over 60,000 units. Homoglycans are polysaccharides composed of identical monosaccharide units like cellulose and starches, particularly amylose. There are also heteroglycans, which contain two or more different monosaccharide units that form complex structures like alginates, guar gums, and so on.

Regarding the properties of polysaccharides, the first important property is solubility because it is very important during the processing of the material, food material containing polysaccharides, etc. So, polysaccharides exhibit diverse solubility behaviors.

□ Properties of polysaccharides

❖ Solubility

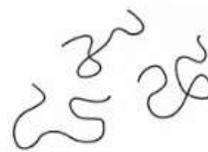
- Polysaccharides exhibit diverse solubility behaviors; some disperse rapidly in water, others remain insoluble, or form swollen particles/globules.
- Solubility influences gelation; some polysaccharides form gels at low concentrations, while others require higher concentrations or do not gel at all.
- Solubility and gelation depend on factors like monosaccharide composition, chemical linkages, hydrogen bonding, ionic interactions, and polymer conformation.
- Hydrogen bonds between hydroxyl groups and water molecules lead to partial immobilization, aiding dissolution or dispersion.
- Linear polysaccharides can form gels through intramolecular hydrogen bonding, while branching or negatively charged groups inhibit this association.
- Linear polysaccharides have higher viscosities than branched ones, and viscosity may vary with pH in polysaccharides containing carboxyl groups.



Some disperse rapidly in water, whereas others remain insoluble or form swollen particles or globules when they come in contact with water. So, the solubility of polysaccharides obviously influences their gelation. Some polysaccharides form gels at low concentrations, while others require higher concentrations to form gels, or there are even certain polysaccharides that do not form gels at all. So, solubility and gelation depend upon factors like monosaccharide composition, chemical linkages, hydrogen bonding, ionic interactions, and polymeric conformation, which is basically the structure of those polymers. Also, hydrogen bonds between hydroxyl groups and water molecules lead to partial immobilization, aiding dissolution or dispersion. So, linear polysaccharides can form gels through intramolecular hydrogen bonding. While branching or negatively charged groups inhibit this association. So, if there is branching, this will create a hindrance to intramolecular hydrogen bonding, etc. So, the linear polysaccharides have higher viscosity than the branched ones and viscosity may vary with pH in the polysaccharide containing carboxyl groups.

❖ Polysaccharide solution, viscosity, and stability

- Polysaccharides (gums, hydrocolloids) are used in foods to thicken, gel, and modify flow properties of liquid and semisolid products.
- Effective at low concentrations (0.25–0.5 %), demonstrating significant ability to increase viscosity and form gels.
- The rotation around glycosidic linkages and chain flexibility influence the conformation, often leading to disordered or random coil states in solution.
- Motion of linear polymer molecules in solution leads to collisions, creating friction and producing viscosity.



Randomly coiled polysaccharide molecules.



The polysaccharide solution, viscosity, and stability are very highly interrelated properties and major properties that govern various reactions and functionalities, etc., during the processing of these materials. So, polysaccharides like gums, hydrocolloids, etc., are used in food to thicken, gel, and modify the flow properties of liquid and similar liquid foods. So, they are very effective at low concentrations, like 0.25 to 0.5 per cent, demonstrating the significant ability to increase viscosity as well as to form gels, that are, these polysaccharides. The rotation around glycosidic linkages and the chain flexibility influences the conformation which often leads to the disordered or random coiled starch in solution. So, you can see that randomly coiled polysaccharides form the solution. The motion of the linear molecules in solution leads to collisions and creates friction, which produces our viscosity or reduces the creation and reduction of the viscosity. Because of the collision and friction, the larger molecules will be broken into smaller ones, and then their viscosity will be reduced.

❖ Factors affecting polysaccharide solution stability

- Most polysaccharides deviate from random coil states, forming stiff coils influenced by monosaccharide composition and linkages.
- Longer, more extended, and rigid polysaccharide molecules generate higher viscosity.
- Viscosity is influenced by the degree of polymerization (DP) and the shape/flexibility of the solvated polymer chain.
- Polysaccharide solutions provide stability and consistency in food and beverage products by controlling texture and flow properties.

Relative volumes occupied by a linear polysaccharide and a highly branched polysaccharide of the same molecular weight.

Then, the factors that affect polysaccharide solution stability include many factors such as the coil states and random coil states forming stiff coils influenced by monosaccharide composition and the linkages they have. The longer, more extended and rigid polysaccharide molecules generate higher viscosity. Viscosity is influenced by the degree of polymerization and the shape or flexibility of the solvated polymer chain. So, polysaccharide solutions provide stability and consistency in foods and beverage products by controlling the texture as well as flow properties of these materials during processing and flow behaviour in the machines, etcetera in the continuous processing.

So, as far as the major polysaccharides found in food, they are starch, hemicelluloses, glycogen, cellulose, pectin, and mucilages and gums. These are the major polysaccharides. Now, one by one, we will take up some important aspects of these polysaccharides.

Starch

- Starch is the primary food reserve in plants, providing 70–80% of global caloric intake.
- Predominantly obtained from cereal grains (corn, wheat, rice) and tubers (potato, cassava).
- Unique chemical and physical properties distinguish starch from other carbohydrates.
- Occurs naturally as insoluble granules, hydrating slightly in cold water and forming low-viscosity slurries.
- Thickening power of starch is activated when granule slurries are heated, forming a high-viscosity paste.
- Composed of two polymers: linear amylose and highly branched amylopectin.



So first, we will talk about starch. It is the primary food reserve in plants, providing about 70 to 80 percent of the global calorie intake in the form of starch, and it is present in grains, etc. These monosaccharide units are polymerized and fused into less reactive polysaccharides, mainly starch, etc., which makes it easier for them to store, cultivate, dry, and perform all those processes. So, these starches are predominantly obtained from cereal grains like corn, wheat, and rice and also from tubers like potato and cassava. They have unique chemical and physical properties. They distinguish starch from other carbohydrates because starch has unique properties. The starches occur naturally as insoluble granules, hydrating slightly in cold water. and forming a low-viscosity slurry. So, when you put some water that is starch in water, it does not dissolve completely rather, it forms some slurry or even a low-viscosity slurry. So the thickening power of starch is activated when these granule slurries are heated. So that is, upon heating, it forms a highly viscous paste. These starches are mainly composed of two polymers: one is the linear unit, that is amylose, and then the highly branched polymer is amylopectin.

So, amylose and amylopectin are the two major polymers. Starch is found in cereal grains. So, amylose is primarily a linear chain of alpha-1,4 linkage, that is, the glucose units are present in the linear form, a linear chain, as you can see here in the structure, and they are joined together with each other by alpha-1,4 linkage.

Amylose

- Amylose is primarily a linear chain of (1→4) linked α-D-glucopyranosyl units.
- Some amylose molecules have branches connected by α-D-(1→6) linkages; branch points are sparse (0.3–0.5%).
- Amylose adopts a right-handed helical shape, with a hydrophobic/lipophilic interior and hydroxyl groups on the exterior.
- Each helix turn contains approximately 6 α-D-glucopyranosyl units.
- Starches generally contain about 25% amylose; high-amylose corn starches contain 50% to 75% amylose.



A trisaccharide segment of an unbranched portion of an amylose molecule. (Ferreira et al., 2007)

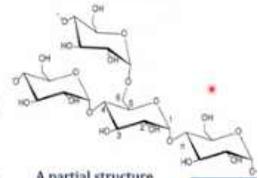


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However, sometimes that is the case if there are branches connected to the alpha D 1 6 linkage. So, branch points are very rare, although this branching is in the amylopectin. However, in the case of amylose, they are completely linear chains. Amylose adopts a right-handed helical shape with a hydrophobic or lipophobic interior and hydroxyl groups on the exterior. So, each helix turn contains approximately 6 alpha D glucopyranosyl units. And starches generally contain about 25% amylose, and this high-amylose corn starches may contain up to even 50% or up to 75% starch. But in general, the food starches or cereal starches contain about 25% amylose in their composition.

Amylopectin

- Amylopectin is a highly branched molecule, with branch points making up 4–5% of total linkages.
- The molecule consists of a main chain with reducing end groups, and multiple branch chains forming clustered double helices.
- Amylopectin has very high molecular weights, ranging from 10^7 (DP ~60,000) - 5×10^8 (DP ~3,000,000), making it one of the largest molecules in nature.
- It constitutes about 75% of most common starches; starches made entirely of amylopectin are known as waxy starches.
- Potato amylopectin is unique for having phosphate ester groups attached at O-6 and O-3 positions, occurring about once in every 215–560 α-D-glucopyranosyl units.



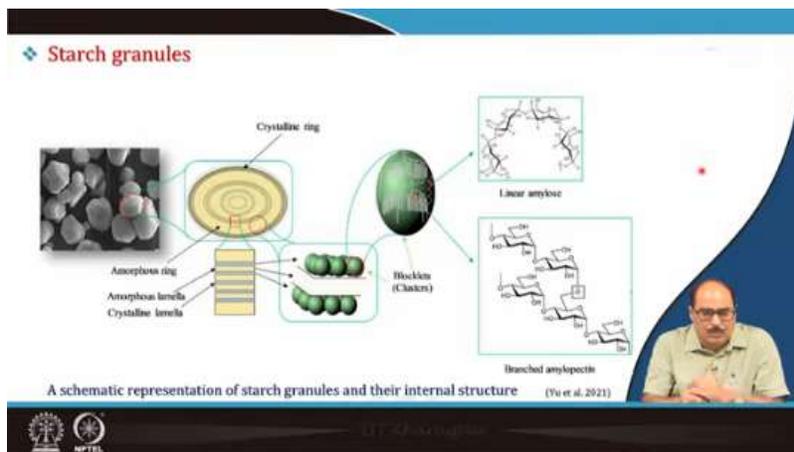
A partial structure of amylopectin (Ong & Ern Jeong, 2019)



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Then comes the amylopectin as you can see here it is a 1, 6 branch that is the amylose unit and when there is another there is a different amylose unit and when they are branched highly, they are branched molecules it is a branched branch occurs up to the 4 to 5 percent of the total linkages. The molecule consists of a main chain with reducing end groups and multiple branch chains forming a clustered molecule. There is a different amylose unit joined with the branched alpha 1 6 linkage that becomes amylopectin. So, amylopectin has

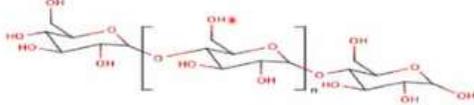
a very high molecular weight ranging from 10^7 to 10^8 multiplied by 10 to the power 8 dp is equal to around 3000,000 making it one of the largest molecules in nature. The cereal starches generally constitute 75%. So, amylopectin, however, starches made entirely of amylopectin are also there, and they are known as waxy starches that are which contain more amount of about 97- 98% or sometimes full amylopectin content. So, potato amylopectin is unique for having fast fast-fed ester group attached at the O 6 or O 3 positions, occurring about once in every 215 to 560. alpha D glucopyranosyl units.



So, here in this picture, I have tried to show you that is how the starch granules, how these starches are present inside the macro material food materials, etcetera are grain inside this is where if you see that what are the There is a, this is presented, there is a crystalline ring, alright. In this, there are amorphous rings, followed by amorphous lamellae, and finally crystalline lamellae. This arrangement illustrates the transition from amorphous lamellae to crystalline lamellae. The lamellar structure is eventually formed by branched amylopectin and linear amylose units. Therefore, these starch granules consist of amylose and amylopectin molecules arranged radially, as shown in the picture. They contain alternating crystalline and non-crystalline amorphous regions. The amylopectins clustered branches form a packed double helix, which create small crystalline lamella, whereas these lamellas are concentrated in the denser layers of the granules, alternating with less dense amorphous layers. The radial ordered structure of starch granules is observable through birefringence, which is visible as a polarization cross where the cross is black under a polarizing microscope. concentrated at the helium. So, they are basically the ordered crystalline molecules, etcetera is there, and when these starches are gelatinized, which we will take up in the later part of the lecture, then the crystallinity is lost, and they become amorphous.

Dextrin

- Dextrins are products of the partial breakdown of starches, with sizes between starches and sugars.
- They exhibit properties that are intermediate between those of starches and sugars.
- Dextrins are formed when starch is subjected to dry heat.
- An example is the toasting of bread, where part of the starch is converted to dextrin.
- The sweet taste of toast is due to the formation of dextrin.



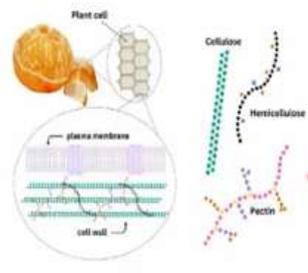
The structure of dextrin
(Parot, 2014)



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Now, we come to the dextrin. So, dextrins are products of the partial breakdown of starches with sizes between starches and granules, and accordingly, they exhibit properties that are intermediate between those of starches and sugars. Dextrins are formed when starch is subjected to dry heat. An example is the toasting of bread. That is, you see when the bread is toasted, it becomes a little sweeter, and that is mainly because during the dry hydrolysis, that is, some portion of the starch. When you toast it, the starch is converted into dextrin, and dextrin has more sweetness than the starch. So, the toasted bread's sweet taste is mainly because of the formation of dextrin and which is the structure of a part of the dextrin molecule.

Plant cell walls' polysaccharides



- Cellulose, hemicellulose, and pectin are interconnected in plant cell walls.
- Pectin** is mainly composed of galacturonic acid (pink hexagons), rhamnose (yellow hexagons), galactose (purple hexagons), and arabinose (orange pentagons).
- Cellulose** is a homopolysaccharide of glucose (green hexagons).
- Hemicellulose** has a main branch of xylose (black pentagons) in which arabinose (orange pentagons) and glucuronic acid (blue hexagons) molecules are attached.

do Amaral Minuzzi et al., 2024



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Then, let us talk about plant cell wall polysaccharides and the plant cell wall. Polysaccharides, as we discussed earlier, are mainly cellulose, hemicellulose, and pectins. They are basically interconnected in the plant cell walls, and you can see here the plant cell

wall is here how this cellulose is arranged, how hemicellulose and pectins are arranged inside the cell wall. So, pectin is mainly composed of galacturonic acids, like the pink hexagons you can see here like these are present. They also include rhamnase, arabinose, and galactose. These are the units that are connected. So, basically, it is a polymer of galacturonic acid. Cellulose is a homopolysaccharide of glucose units, like the green hexagons. Hemicellulose has a main branch of xylose, which is the black pentagon, to which arabinose and glucuronic acid molecules are attached. So, cellulose is similar to starch, but here, instead of alpha-1,4 branching, it has a different branching pattern. In fact, the human system cannot digest it, as it lacks alpha-1,6 and 1,4 branching; rather, it has a beta system. It does not have alpha 1,6 and 1,4 branching. Rather, it has beta linkages instead of alpha.

Pectic substances

- Pectic substances are found in plant cell walls and the middle lamella, acting as a cementing material to hold cells together.
- They are mixtures of polysaccharides, primarily formed from galacturonic acid, galactose, and arabinose.
- The water-insoluble parent substance protopectin during fruit ripening, leading to an increase in soluble pectin.
- Pectinic acid, derived from protopectin, forms a colloidal solution and can gel with sugar and acid.
- Commercial pectin is extracted from citrus peels or apple pomace; high methylation (>50%) is necessary for rapid jelly setting.

Various pectic substances

(Satapathy et al., 2020)

Then, pectic substances are found in plant cell walls and the middle lamella. That is, they act as a cementing material to hold the cells together. There are pectic substances; it is a generic nomenclature that includes four major groups protopectin, pectic acid, pectinic acid, and pectins. So, these collectively are known as pectic substances. Normally, these pectic substances or pectins are mixtures of polysaccharides primarily formed from galacturonic acid, galactose, and arabinose. The water-insoluble parent substance, protopectin, during fruit ripening leads to an increase in the soluble pectin. Meanwhile, pectinic acid, which is derived from protopectin, forms a colloidal solution and can form a gel with sugar and acids. In fact, commercial pectin is extracted from citrus peels or apple pomace, etc., and it should have a high degree of methylation, that is, more than even 50%. is necessary for rapid jelly setting, etc. So, it is the pectin and its ability to form a gel in the

presence of proper acid and in the presence of appropriate sugar content and water content, and this is this property which is used for making jam, jelly, marmalade, and other products.

Cellulose

- Cellulose constitutes over 25% of cell walls in higher plants and accounts for nearly half of the world's carbon supply.
- Found in woody tissues as partially crystalline microfibrils; in vegetable pulp, it has little fibrous character.
- Embedded in an amorphous gel of hemicellulose and pectic substances, influencing the texture of fruits and vegetables during ripening, storage, and processing.
- Composed of long chains of glucose residues with β -(1 \rightarrow 4) linkages, giving it a very high molecular weight.
- Insoluble in water and not digested by humans, cellulose serves as dietary fiber or roughage.
- Can be broken down into glucose by microbial enzymes, such as those in the rumen of animals.

Structure of cellulose

(Ghoshalvadeh & Alim, 2013)

Then, cellulose constitutes over 25% of the cell wall in higher plants and accounts for nearly half of the world's carbon supply. It is found in woody tissues, in partially crystalline microfibrils, in vegetable pulp; it has little fibrous character. It is found embedded in an amorphous gel of hemicellulose and pectic substances which finally influences the texture of fruits, vegetables, etc., during ripening, storage, and processing. So, these celluloses are composed of chains of glucose residues, as I told you earlier, beta 1-4 linkages, giving it a highly very high molecular weight, and the human body does not have the molecular machinery to break this beta 1-4 linkage, and that is why it becomes an indigestible substance. However, it is a very important material from the nutrition point of view because it acts as roughage. It also provides dietary fiber. So, it aids in the excretion process. So, in order to keep us healthy and well, these celluloses and dietary fibres are very important. It can be broken down into glucose by microbial enzymes, such as those which are present in the remains of animals.

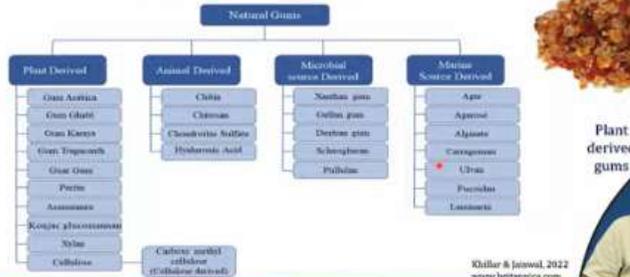
Hemicelluloses, similarly, are also a diverse group of polysaccharides found in land plants, excluding cellulose, starch, and pectic substances. These are substances other than cellulose, starch, and pectic substances. They are insoluble in water but soluble in alkali. They are composed of various sugars, including pentoses, hexuronic acids, and occasionally also rhamnose. They function to cement cellulose microfilaments together, contributing to plant cell wall structure. It forms part of the undigested carbohydrate and also serves as dietary fiber.

Hemicelluloses

- Hemicelluloses are a diverse group of

Gums

- Hydrophilic substances with high molecular weight forming viscous solutions or dispersions in water.



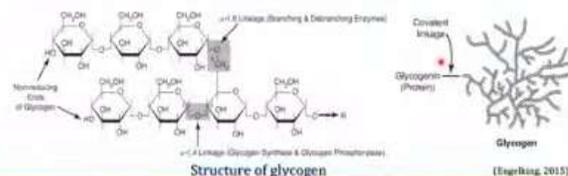
Killar & Jaiswal, 2022
www.livestack.com

Then is called starch, which is the storage polysaccharide found in animal cells.

glycogen animal

Glycogen

- Storage polysaccharide in animals, often referred to as "animal starch."
- Predominantly found in the liver and skeletal muscle.
- Rapidly hydrolyzes to D-glucose after slaughter.
- Resembles amylopectin but is more branched than amylopectin.

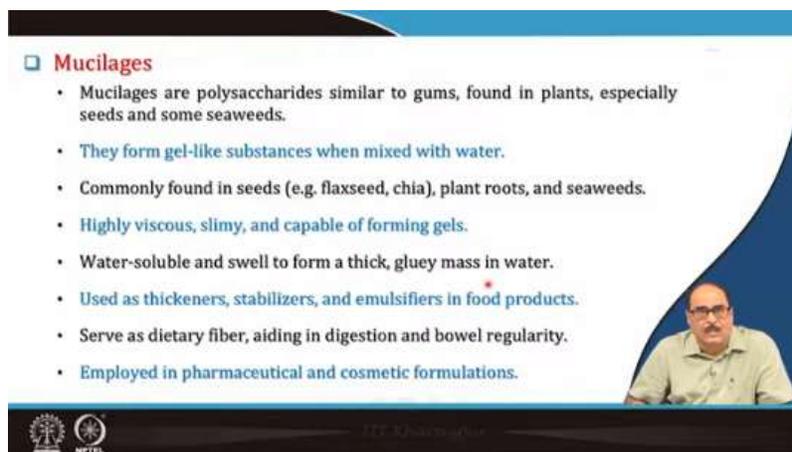


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It is predominantly found in the liver and skeletal muscle. It rapidly hydrolyzes to glucose after the animal is slaughtered, and it resembles amylopectin. Like in the branching phenomena as well, but it is rather more branched than amylopectin, right.

So, these are gums; these are hydrophilic, again polysaccharide, hydrophilic substances with high molecular weight forming various solutions or dispersions in water. And there are various natural gums like plant-derived gums: gum arabic, gum ghatti, gum karaya, gum tragacanth, guar gum, pectin, xylan, cellulose, etc. These are the plant-derived gums. Similarly, Animal-derived gums are chitin, chitosan, and hyaluronic acid. Microbial-derived gums like xanthan gum, xylan gum, dextran gum, even marine sources-derived gums like agar, agarose, alginate, fucoidan, laminin, all those things.

So, these are various plant-derived as well as animal-derived or microbial-derived gums. And these gums are basically polysaccharides. They have various properties in the food material in many food processes and are used as a thick gravy thickener. They are used as a moisture retention agent, as a moisture dehydrating agent, and for many purposes, such as a filtering agent or thickening of gravy, sausage, etc. For various purposes, there are several. It is a big industry's ingredient; they are made and defined for use in food products for improving various functional properties, capability, and many other even carboxymethyl cellulose, etc. It is derived from cellulose and has various functional applications in different foods.



Mucilages

- Mucilages are polysaccharides similar to gums, found in plants, especially seeds and some seaweeds.
- They form gel-like substances when mixed with water.
- Commonly found in seeds (e.g. flaxseed, chia), plant roots, and seaweeds.
- Highly viscous, slimy, and capable of forming gels.
- Water-soluble and swell to form a thick, gluey mass in water.
- Used as thickeners, stabilizers, and emulsifiers in food products.
- Serve as dietary fiber, aiding in digestion and bowel regularity.
- Employed in pharmaceutical and cosmetic formulations.

Then mucilages, they are polysaccharides similar to gums found in plants, especially seeds and some seaweeds. They form gel-like substances when mixed with water, commonly found in seeds like flaxseed and chia seeds, as well as in plant roots and seaweeds. They are highly viscous, slimy, and capable of forming gels. They are water-soluble and swell

to form a thick glue-like mass in water. They are used as thickeners, stabilizers, emulsifiers, etc., in food products. They serve as dietary fiber aiding in digestion and bowel regularity. They are also used in pharmaceutical and cosmetic formulations.

Starch gelatinization

- **Cold water interaction:** Starch granules are insoluble but can absorb water reversibly, swelling slightly and returning to their original size upon drying.
 - ✓ Gelatinization occurs when starch is heated in water.
 - ✓ There is disruption of molecular order within starch granules.
 - ✓ Irreversible swelling, loss of birefringence, and loss of crystallinity occurs.
 - ✓ Amylose leaching begins during gelatinization, though some leaching can occur prior to the process.
 - ✓ Gelatinization occurs over a temperature range, varying by starch type, water ratio, and granule heterogeneity.
 - ✓ Key temperatures are onset, peak and conclusion temperature, which corresponds to significant changes occur in the structure of starch.

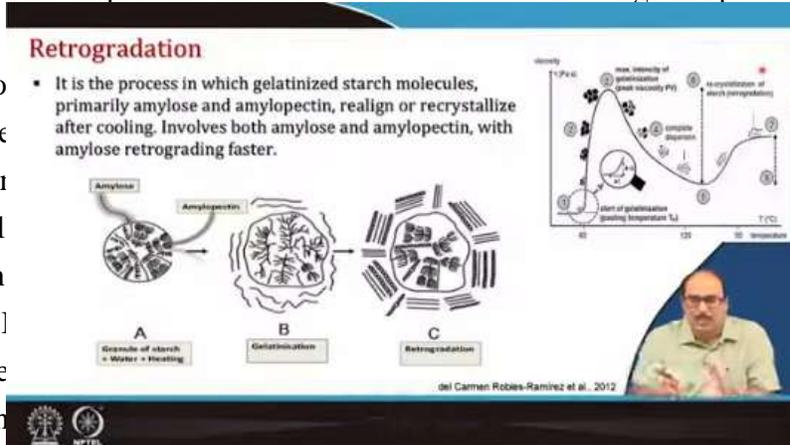
Process of starch gelatinization

www.fdinachemistry.com

So, there are various applications of mucilages. Now, let us talk about very important properties, that is, the properties of these starches and pectins, etc. We take up the two major components like starch and pectin in the fruits and vegetables, and starch in the food grains. So, in fact, when food grains are processed, even during dough-making in bakery products or other products, these starches undergo changes. For example, when you take rice and cook it, the starch inside undergoes various processes. These changes in starch are understood in the form of gelatinization and retrogradation, which actually regulate the processing and other characteristics, and also provide various functional properties in the grains, etc. Similarly, changes in pectic substances lead to structural changes. And all those things in the fruits and vegetables. So, starch will let us see starch gelatinization. So, what happens if you put some starch in water? It will not dissolve. Rather, the starch molecule will absorb water, and it will swell in aggregate size, swell in aggregate, and if you further heat it, it will take more water, and a point will come where it will rupture. It will collapse and form a paste-like material. This entire process is called gelatinization. That is, starch granules are insoluble in water, but they can absorb water reversibly as they swell slightly and return to their original shape upon drying. That is, after it collapses into a paste, if you dehydrate it again, then water can be removed, and the starch will return to its original shape. So, this is the cause of gelatinization, particularly when the starch is heated in water. If excess water is present, then, as I told you, a point will come where you can see that this abrupt increase in the rate of water absorption occurs, and then this abrupt increase at that point starch will start losing its property of the crystallinity, that is it is also it loses its

crystallinity, it loses its birefringent property. And finally, that is, it will come to a point when it almost has lost all its crystallinity, its birefringent property, and it starts its solution in a collapses form space. and it becomes a thick or thin gel depending upon the characteristics

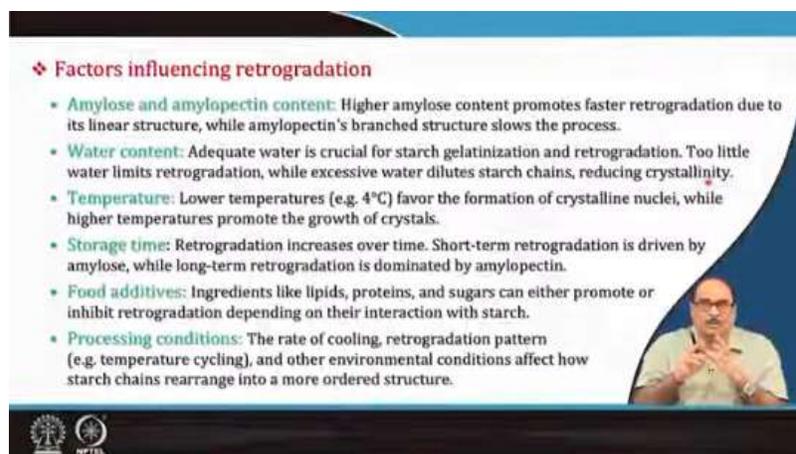
gelatinization o and irreversible amylose leachi process as well initially, when gelatinization.] the range of the different starch



gelatinization temperature is used to identify the sources of the starch. It occurs over a temperature range, and key temperature are onset temperature, as you can see here that is, this is the start when it is heated, only the start of gelatinization, and then it will come here that is, number 2—the gelatinization temperature is increasing, it is taking moisture, granules are swelling, etcetera, and then finally comes the maximum intensity that is, peak viscosity is obtained here. And then there is a collapse; it forms a paste. After that, again, if you come to this point, this is up to gelatinization. And then, in reverse, when you go, it will become retrogradation—that is, changes in signature changes occur in the structure of starch.

Then comes retrogradation that is, when it is cooked and starch, if it is again now has gelatinized, and if it is further heated, then if there is sufficient moisture present, there will be further that is, it may swell may continue further if there is sufficient water available. This additional swelling may result in an increase or decrease in the viscosity of the material because there are these swollen granules that try to collide frequently, and the zigzag motion is there, and because of this collision, larger molecules are broken down and that cut. So that depends upon the various factors like temperature, concentration, and even other factors which might be present in the system. Then after that, what happens if you cool it down? Allow it to cool uninterrupted, then those hydrogen bonds etcetera which were broken, the other bond broken during the process of gelatinization, they try to reform again, alright. That is the starch molecule primarily amylose and amylopectin, they realign or recrystallize after cooling.

Here both amylose and amylopectins are involved, but in the amylopectin, this branch prevents the reformation of the bonding, etcetera hydrogen bonds reformation. So, amyloses retrograde at a higher rate faster rate than amylopectin, but definitely when it is allowed to cool. Depending upon how much amylose or amylopectin is, it will form a soft or thick hard or soft gel. If there is less amylopectin and more amylose, it may form a little thick gel and a strong gel. Amylopectin will result in a soft gel. So that is the process of, you can say, recrystallization, etcetera, and the point where it comes upon reform. It is a process where it cools down and then undergoes retrogradation. So, gelatinization and retrogradation both have very important functionalities to play, particularly in bakery products, functional products, or any food where these starches are used, grain flours, etc., are used. So, they regulate the process.



❖ **Factors influencing retrogradation**

- **Amylose and amylopectin content:** Higher amylose content promotes faster retrogradation due to its linear structure, while amylopectin's branched structure slows the process.
- **Water content:** Adequate water is crucial for starch gelatinization and retrogradation. Too little water limits retrogradation, while excessive water dilutes starch chains, reducing crystallinity.
- **Temperature:** Lower temperatures (e.g. 4°C) favor the formation of crystalline nuclei, while higher temperatures promote the growth of crystals.
- **Storage time:** Retrogradation increases over time. Short-term retrogradation is driven by amylose, while long-term retrogradation is dominated by amylopectin.
- **Food additives:** Ingredients like lipids, proteins, and sugars can either promote or inhibit retrogradation depending on their interaction with starch.
- **Processing conditions:** The rate of cooling, retrogradation pattern (e.g. temperature cycling), and other environmental conditions affect how starch chains rearrange into a more ordered structure.





There are various factors that influence gelatinization and, finally, retrogradation, which includes amylose and amylopectin content. Higher amylose content, as I told you, promotes faster retrogradation due to its linear structure, while amylopectin's branched structure slows the process. Then, water content also plays a role. Adequate water is crucial for

starch gelatinization and retrogradation. Too little water limits retrogradation, while excess water dilutes starch chains, reducing crystallinity. Temperature also matters. Lower temperatures, for example, 4 degrees Celsius, favour the formation of crystalline nuclei, whereas higher temperatures promote the growth of crystal storage time, even when retrogradation increases over time. Short-term retrogradation is driven by amylose, while long-term retrogradation is dominated by amylopectin. The presence of certain food additives and ingredients like lipids, proteins, and sugars can either promote or inhibit retrogradation depending upon their interaction with the starch. Also, the processing conditions like the rate of cooling. Retrogradation pattern, temperature cycling, etc and other environmental factors affect how this chain energy or chain rearranges into a more orderly structure. So, these are the various factors that will influence retrogradation.

❖ Impact of retrogradation

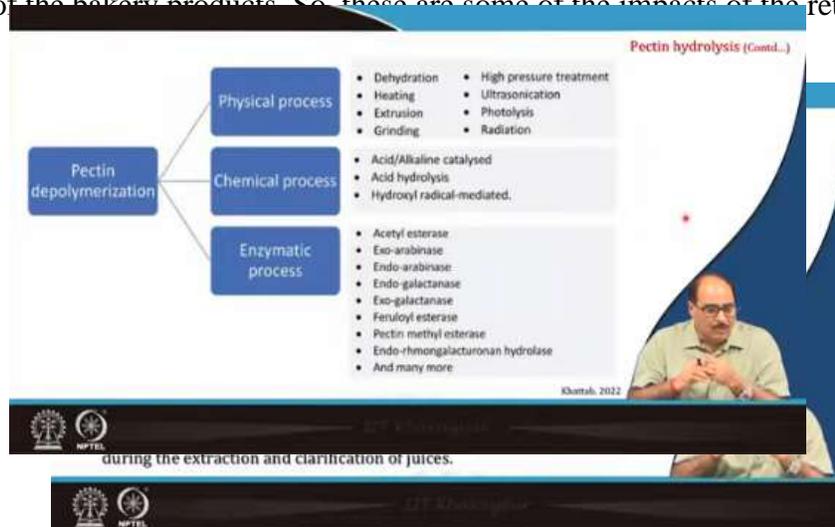
- Starch retrogradation can negatively impact the quality of starchy foods by altering their texture, flavor, and nutritional value
- ✓ **Bread staling:** Crumb firmness increases, freshness perception decreases.
- ✓ **Baked goods:** Starch transitions from amorphous to crystalline state post-baking.
- ✓ **Shelf life:** Surfactants like GMP (Glyceryl monostearate) and SSL (Sodium stearyl lactylate) are added to delay staling and extend shelf life.
- ✓ **Retrogradation** also contributes to lowering the shelf-life of starchy food.

The diagram illustrates the starch structure in bread at three stages: **Dough Stage** with a **Crystalline structure**, **Fresh Bread** with a **Gelatinized starch: Amorphous structure**, and **Stale Bread** with **Retrograded starch: Recrystallized structure**. A small video inset shows a man speaking.

<https://biologystreader.com/>

Then impact of retrogradation if you see as I already gave that is in the various products like bread staling, baked goods, even their storage life, all those retrogradation contributes even to lowering the shelf life of starchy food. In the bread staling that is crumb firmness increases, freshness, perception decreases etc. Particularly when the bread is kept inside a refrigerator, you see there may be some retrograde, etc., and bread steals and some sort of that flavor unpleasant flavor, that is, you can say. In the dough stage, the starch molecule has a crystalline structure, and then fresh bread, when it is baked and taken out of the oven, contains gelatinized starch with an amorphous structure only. And then when if you take it out, that is as soon as the bread is out of the oven. oven, it starts staling, the retrogradation process starts and when this retrogradation occurs at a higher rate if the bread is kept in the refrigerator. So, maximum staling is at less than 20 degrees Celsius temperature. So this results in crumbliness, which is the crumbly grain, leathery crust, and some stale flavour developing. However, these staleness can be reversed if the bread is again further toasted

etc. So, in the baked group, the starch transitions from an amorphous to a crystalline state. In post-baking, that also influences their texture, flavour as well as nutritional value. Surfactants like glycerol, monostearate and SSL are added to delay staling and the extended shelf life of the bakery products. So, these are some of the impacts of the retrogression.



Then we will talk about briefly pectin hydrolysis that is the pectins we have seen earlier. They are the high molecular weight hetero poly polymers that contain a high content of galacturonic acid and that is an oxidized form of D-galactose which constitutes the main monomeric unit around 65 per cent of the peptide molecule. So, it provides structural integrity and also rigidity to plant tissue. So, when the fruit is firm, it is basically peptide, and then it gives firmness to the fruit tissue. So, the structure of pectin can change according to the material of origin. Hydrolysis is a chemical process. Earlier. We have already discussed in detail how hydrolysis takes place. So, hydrolysis of the pectin is broken down into constituent monomers and this process involves cleavage. of the glycosidic bonds in the pectin polymer chain. So, pectin hydrolysis can be carried out either by acid or enzymatic method. Acid methods are commonly used in analytical procedures. So, these enzymatic procedures are also widely used in industry to improve the yield during extraction and clarification of the juices, etc.

So, the peptin depolymerization there are physical process, chemical process and enzymatic process like dehydration, heating, extrusion, acid, alkali or even exo-arabinase, endo-arabinase.

All these various factors influence the characteristics of fruits, vegetables, and other materials.

Pectin hydrolysis (Contd...)

- ❖ **Factors influencing hydrolysis**
 - ✓ **pH Levels:** The rate of hydrolysis is significantly influenced by the acidity or alkalinity of the environment.
 - ✓ **Temperature:** Higher temperatures accelerate the hydrolysis process.
 - ✓ **Time:** The extent of hydrolysis increases with prolonged exposure to the catalytic conditions (acidic or enzymatic).
- ❖ **Applications of pectin hydrolysis**
 - ✓ **Food Industry:** Hydrolyzed pectin is used to modify the texture of food products, create low-methoxyl pectin for use in low-sugar jellies, and improve the gelling properties of pectin.
 - ✓ **Nutraceuticals:** Produces bioactive fragments with potential health benefits, such as promoting gut health.



pectin, and this process may cause changes during ripening. In other courses, we will see how pectin

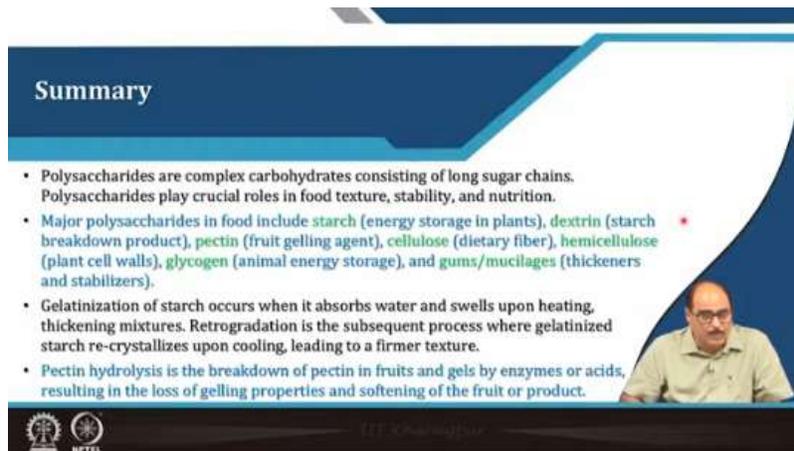
Pectin hydrolysis (Contd...)

- ❖ **Acid hydrolysis**
 - ✓ **Catalyst:** Typically occurs in the presence of acids such as hydrochloric acid (HCl) or sulfuric acid (H₂SO₄).
 - ✓ **Process:** The acid breaks down the glycosidic bonds in the pectin molecule, converting it into smaller oligosaccharides, disaccharides, and ultimately galacturonic acid.
- ❖ **Enzymatic hydrolysis**
 - ✓ **Catalysts:** Pectinases are the enzymes involved, including polygalacturonase, pectin lyase, and pectin esterase.
 - ✓ **Process:** These enzymes specifically target and break the glycosidic bonds, facilitating the depolymerization of pectin.
 - ✓ **Outcome:** Results in the production of galacturonic acid and various oligosaccharides.



So, like acid hydrolysis and enzymatic hydrolysis, what is the catalyst for all these processes? Acid hydrolysis breaks down the glycosidic bonds in the pectin molecule, converting it into smaller oligosaccharides or disaccharides. Similarly, enzymatic hydrolysis occurs. Enzymes like polygalacturonase, pectin lyases, or pectin esterase are involved. Pectin methyl esterase demethylate pectin; these enzymes also break glycosidic bonds, resulting in the production of galacturonic acid and various oligosaccharides.

There are various factors that influence hydrolysis, such as pH levels, temperature, and even the time of the reactions. These factors, like higher temperature, will accelerate the hydrolysis process. More time means more hydrolysis. pH, which is the acidity or alkalinity of the environment, will influence the hydrolysis rate of the hydrolysis reaction. So, the application of pectin hydrolysis, as I told you, is very important. In the food industry, hydrolyzed pectin is used to modify the texture of food products, create low-methoxy pectin for use in low-sugar jellies and improve the gelling properties of pectin. Nutraceuticals also produce bioactive fragments with potential health benefits, such as promoting gut health and all those things.



Summary

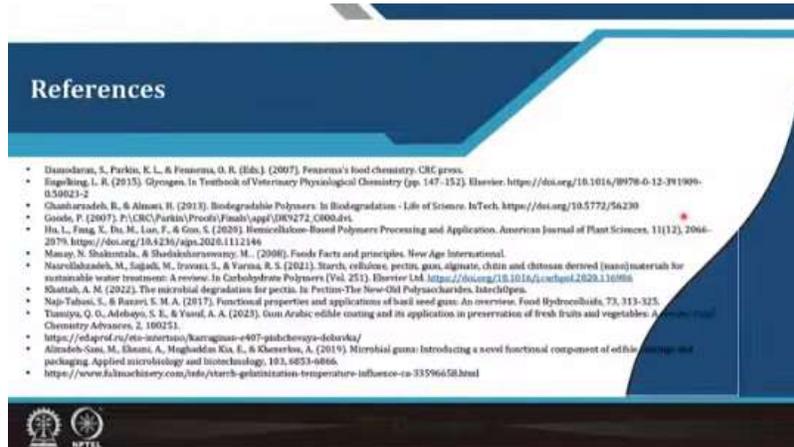
- Polysaccharides are complex carbohydrates consisting of long sugar chains. Polysaccharides play crucial roles in food texture, stability, and nutrition.
- Major polysaccharides in food include starch (energy storage in plants), dextrin (starch breakdown product), pectin (fruit gelling agent), cellulose (dietary fiber), hemicellulose (plant cell walls), glycogen (animal energy storage), and gums/mucilages (thickeners and stabilizers).
- Gelatinization of starch occurs when it absorbs water and swells upon heating, thickening mixtures. Retrogradation is the subsequent process where gelatinized starch re-crystallizes upon cooling, leading to a firmer texture.
- Pectin hydrolysis is the breakdown of pectin in fruits and gels by enzymes or acids, resulting in the loss of gelling properties and softening of the fruit or product.

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So finally, I will summarize this lecture by saying that these polysaccharides are complex carbohydrates consisting of large sugar chains. Polysaccharides play a crucial role in food texture, stability, as well as in nutrition. The major polysaccharides present in food are starch, which is the major energy-giving and energy storage in plants. Dextrin, which is starch breakdown products, or fruit gelling agents like pectin, dietary fibre cellulose, and hemicellulose, which is present in the plant cell wall or animal energy storage glycogen or even gums and mucilages, which are thickeners and stabilizers used in various processed foods. Then, gelatinization and retrogradation are the two major phenomena that these starches undergo, particularly when they are heated in the presence of water, and this

influences and improves the characteristics and regulates the food processing operations. The breakdown of pectin by enzymes or acids, results in the loss of gelling properties, softening of the fruit product, fruits, or product, etc.

So, these are the references used in this lecture.



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Thank you very much for your patient hearing. Thank you very much.

