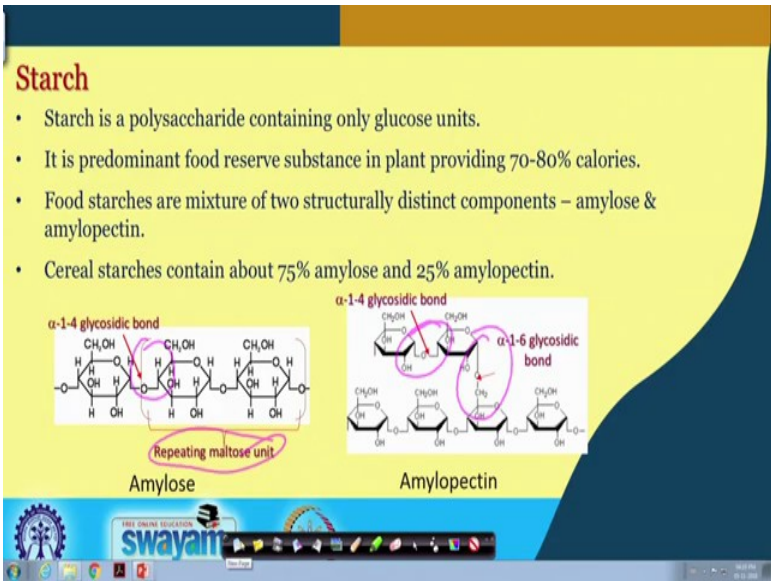
Novel Technologies for Food Processing and Shelf Life Extension
Prof. Hari Niwas Mishra
Department of Agricultural and Food Engineering
Indian Institute of Technology, Kharagpur

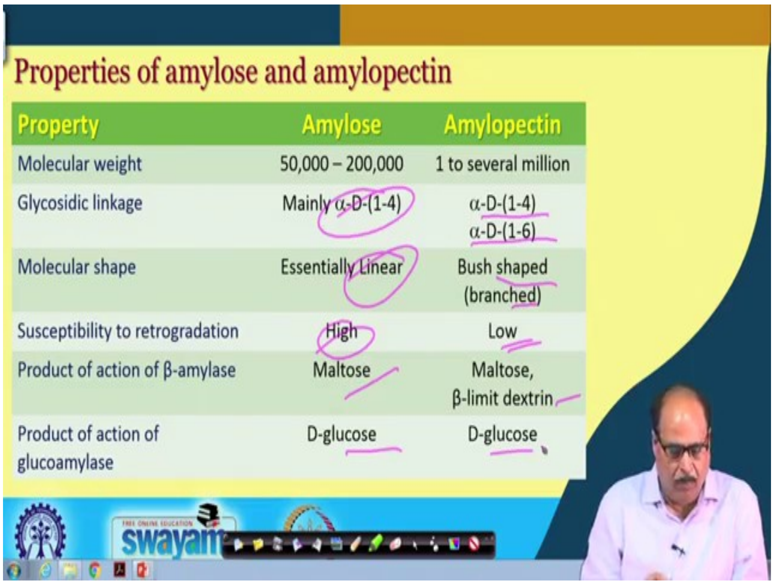
Lecture - 05
Gelatinization & Retrogradation of Starch

In this lecture, a very important aspect of food reactions which normally occur in starch-containing foods i.e. gelatinization and retrogradation processes are discussed.



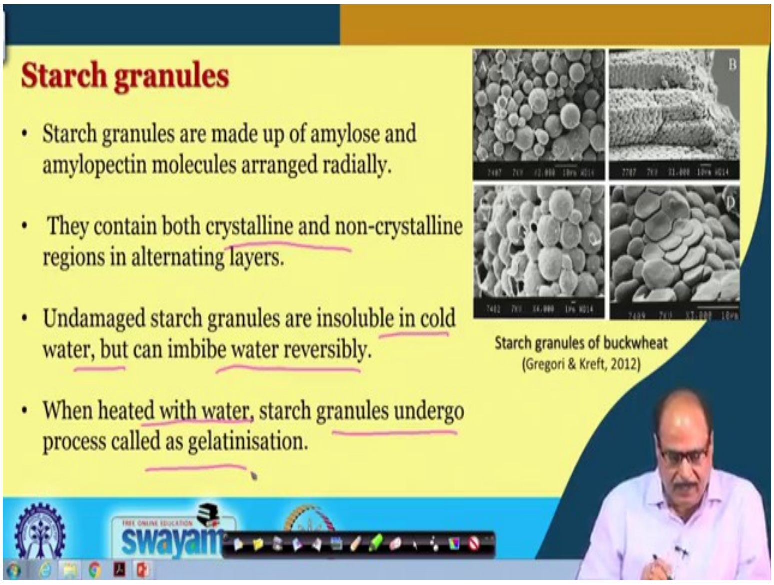
Starch

Starch is a polysaccharide containing glucose units. It is a predominant food reserve substance in plant and it provides about 75 to 80 % of the calories in the food. Food starches are a mixture of two structurally distinct components and those are amylose and amylopectin. Cereal starches, on an average, contain about 75 % amylose and 25 % amylopectin. Amylose is a linear chain of repeating maltose unit where glucose units are joined by α-1-4 glycosidic linkages. The amylopectin molecules are branched chain having both α-1-4 and α-1-6 glycosidic linkages. Individual chains are joined with α-1-4 linkage whereas, the branches are joined by the α-1-6 linkages.



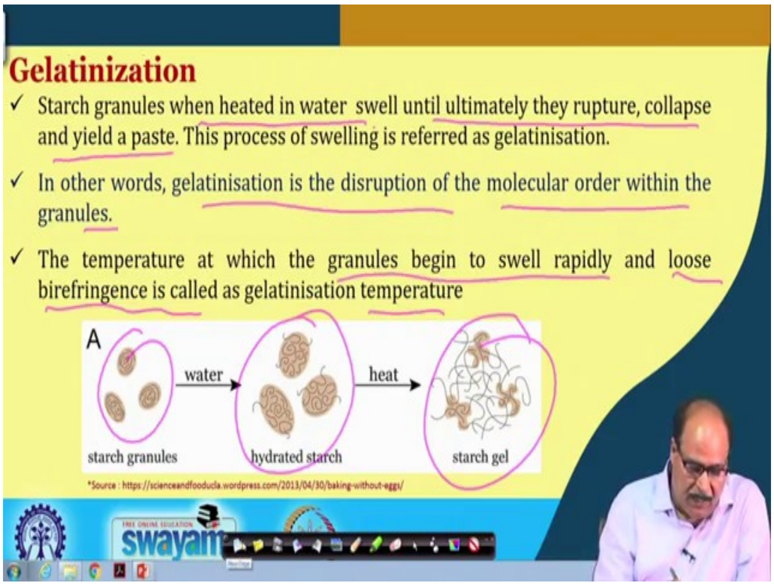
Properties of amylose and amylopectin

The comparison of the properties of amylose and amylopectin is shown in the Table. The molecular weight of amylose ranges between 50000 to 200000 whereas that of amylopectin ranges from 1 to several million. The glycosidic linkage in amylose is mainly α-1-4 whereas, in the amylopectin, it is both α-D-1- 6 and α-D-1-4 linkages. The molecular shape of amylose is essentially linear whereas, the amylopectin is bush shaped or branched. Amylose has a high susceptibility to retrogradation whereas, amylopectin has comparatively low susceptibility to retrogradation. The action of β-amylase releases maltose and β-limit dextrin from the amylopectin, but from the amylose, it gives only maltose. Product of action of glucoamylase is D-glucose in both the cases.



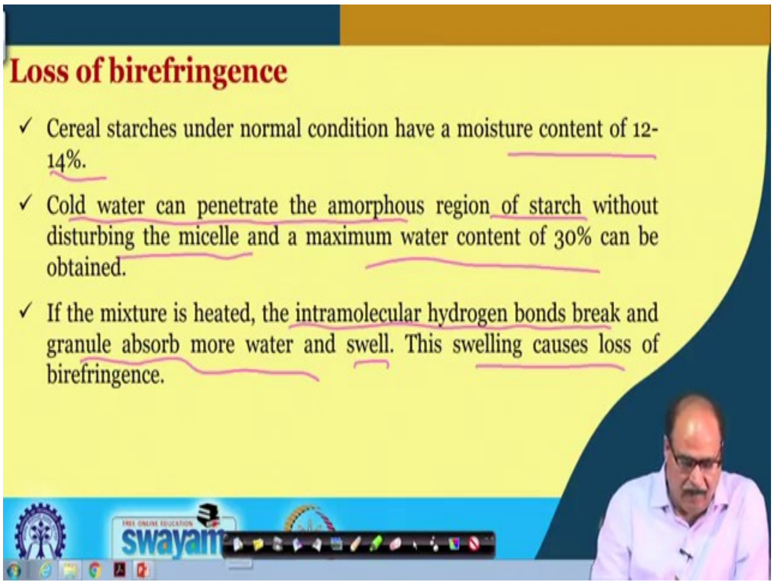
Starch granule

The starch granules are made up of amylose and amylopectin molecules which are arranged radially (See Fig.). They contain both crystalline as well as non-crystalline regions in alternating layers. Undamaged starch granules are insoluble in cold water, but they can imbibe water reversibly i.e. they can absorb water, but upon drying they further shrink and come to their original stage. When heated with water, starch granules undergo a process that is known as gelatinization i.e. they absorb water and swell.



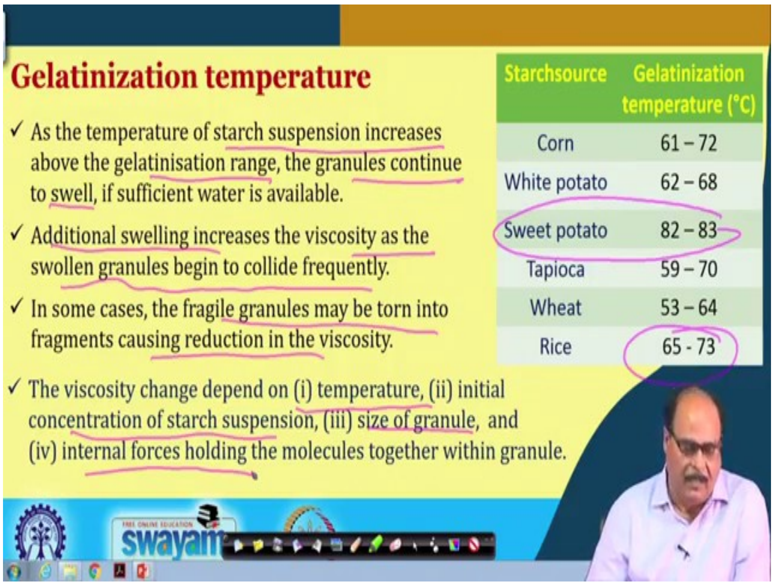
Gelatinization

Gelatinization can be defined as the process in which the starch granules when heated in water swell until ultimately they rupture, collapse and yield a paste. In other words, gelatinization is the disruption of molecular order within the granules. It can be seen in Fig. that the starch granules are present in the intact grains or in other materials. When they are soaked in the water, water penetrates, fills up the micellar region and the starch granule swells and upon heating, it results in the formation of a starch gel. The temperature at which the granules begin to swell rapidly and lose their property of birefringence is called gelatinization temperature. However, the gelatinization temperature is not a single temperature, it is a range of temperature and is the characteristic of the material.



Loss of birefringence

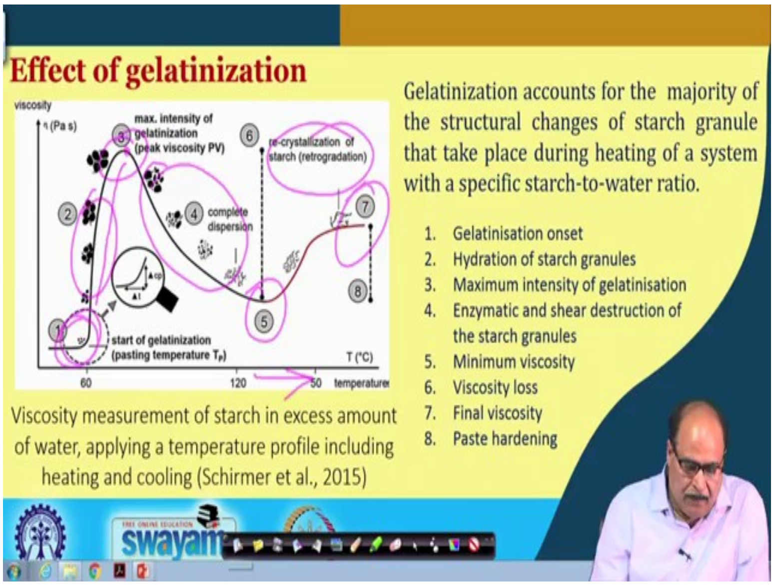
Cereal starches under normal conditions have a moisture content of about 12 to 14%. The grain when soaked in water, if sufficient amount of water is present, the cold water penetrates the amorphous regions of the starch without disturbing the micelles and maximum water content of up to 30 % can be reached within the grain. If the mixture is heated, the intramolecular hydrogen bonds break and granules absorb more water and swell. This swelling causes a loss of birefringence.



Gelatinization temperature

In this figure, the gelatinization temperature ranges of different materials are given. The gelatinization temperature range is used to characterize the source of starch e.g. for sweet potato, the gelatinization temperature is in the range of 82 to 83 °C. That means, it is a very narrow gelatinization range, its swelling starts at 82 °C and gelatinization completes at 83 °C. Whereas, the gelatinization of starches in rice starts at 65 °C; it takes a little longer temperature to complete the gelatinization process which completes at 73 °C.

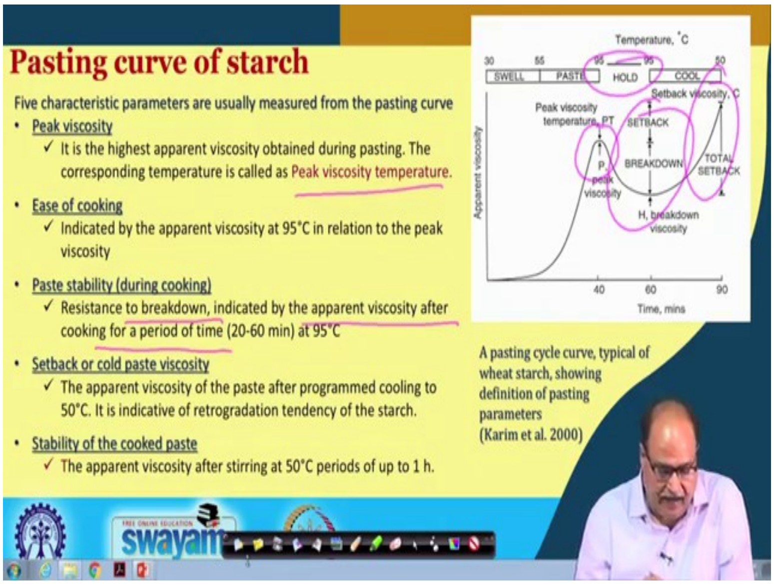
As the temperature of the starch suspension increases above the gelatinization range if sufficient water is present, the granules continue to swell and this additional swelling increases the viscosity as swollen granules begin to collide frequently. In some cases, the fragile granules may be torn into the fragments causing a reduction in the viscosity. The viscosity change will depend upon temperature, initial concentration of the starch suspension, size of the granules and internal forces holding the molecules together within the granules.



Effect of gelatinization

In this slide, the effect of temperature on the viscosity of the starch suspension is shown. At a particular temperature, the gelatinization process starts that is called as the pasting temperature (T_p). Further increasing the temperature, if sufficient water is present, it results into the increase in the viscosity due to hydration of the starch granules and finally, it reaches to point 3 which has a maximum intensity of gelatinization and the viscosity at this point is known as peak viscosity (P_v).

Further increase in the temperature, if sufficient water is present, then there comes stage 4, where the complete dispersion of starch occurs i.e. enzymatic and shear destruction of the starch granules takes place and finally, the viscosity comes to the minimum point. At this point, the temperature is reduced and subsequently, the recrystallization or retrogradation of starch takes place. In the end, it reaches to the final viscosity at point 7 and then further cooling results into the paste hardening. This is the process of the gelatinization which accounts for the majority of the structural changes of starch granules that take place during heating of a system with a specific starch to water ratio.



Pasting curve of starch

In a similar way, the pasting curve of the starch can be discussed.

(i) Peak viscosity: It is the highest apparent viscosity obtained during pasting and the temperature corresponding to this point is called peak viscosity temperature (PT).

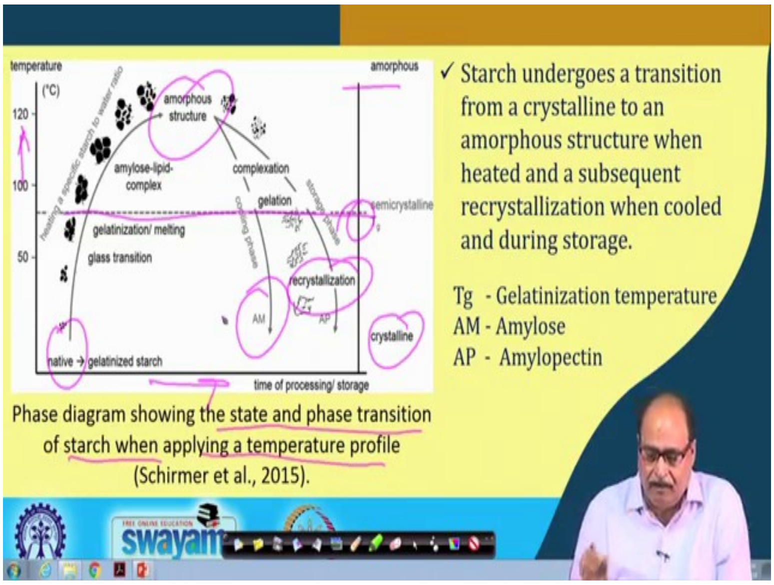
(ii) Ease of cooking: It is indicated by the apparent viscosity in relation to the peak viscosity.

(iii) Paste stability: The paste stability is related with resistance to breakdown which is indicated by apparent viscosity after cooking for a period of 20 to 60 min at 95 °C.

(iv) Setback or cold paste viscosity: It is the apparent viscosity of the paste after programmed cooling to 50 °C which is an indicative of retrogradation tendency of the starch.

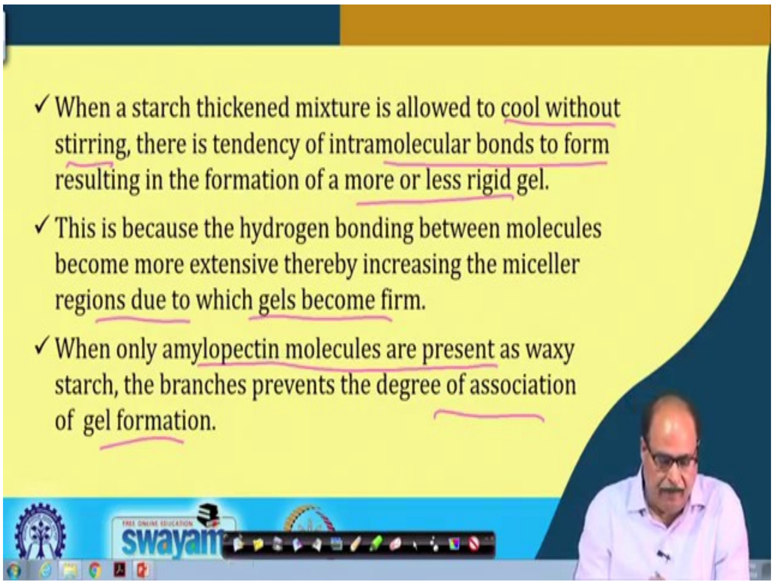
(v) Stability of the cooked paste: Finally, the apparent viscosity after stirring at 50 °C periods for up to 1 h gives the total setback.

The pasting characteristics of the starch material can be evaluated by using the instrument Rheometer/Rapid Visco Analyser.

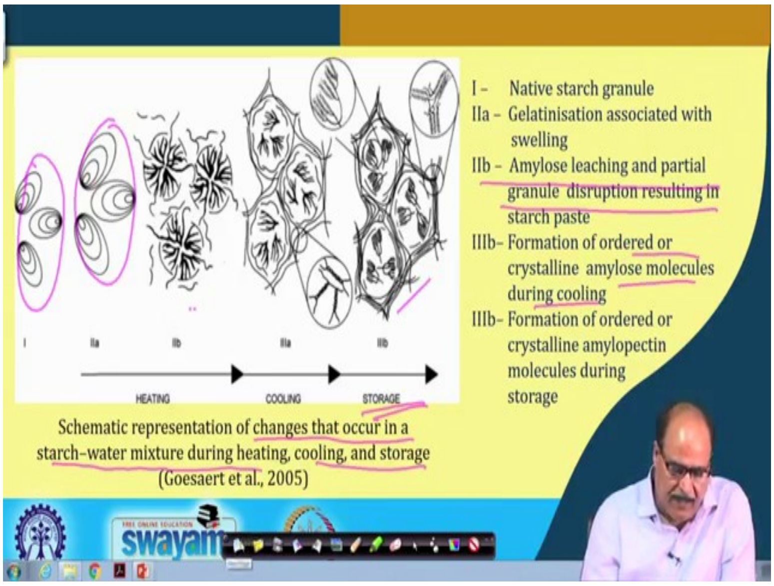


The figure shows the phase diagram showing the state and phase transition of starch when applying a temperature profile. In this, y-axis represents the temperature rise and x-axis represents the time of processing or storage.

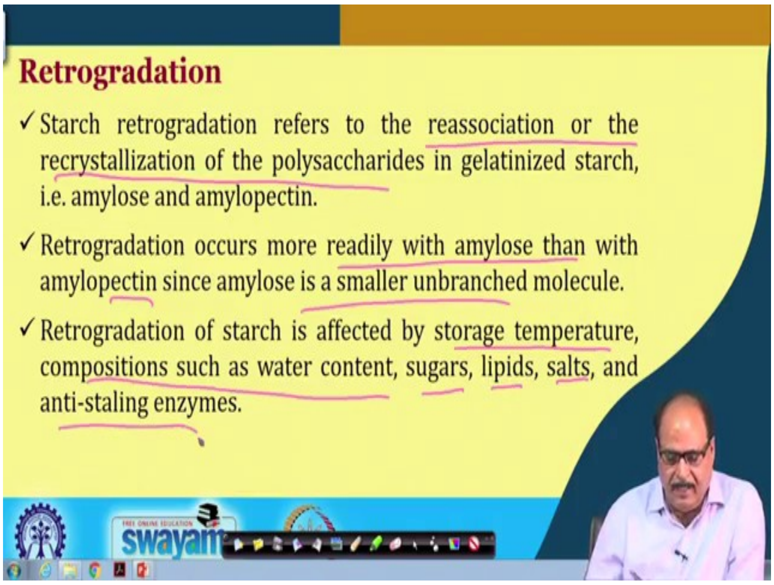
Initially, with the increase in the temperature and duration of the processing (like cooking and other process when heat is applied), the native starch is changed into the gelatinized starch and comes to a stage of glass transition in which it is in the semi-crystalline form. Initially, it is crystalline, but with the passage of time and temperature, the starch structure changes to the amorphous structure and if it is further cooled or stored in a given time, then there may be complexion, gelation processes or even the recrystallization process. In the recrystallization process, during cooling the amylose complexes easily retrograde than that of the amylopectin whereas the recrystallization of the amylopectin is normally taken place during the storage.



When a starch-thickened mixture is allowed to cool without stirring, there is a tendency of intramolecular bonds to form resulting in the formation of a more or less rigid gel. This is because the hydrogen bonding between the molecules become more extensive thereby increasing the micellar region due to which gels become more firm. When only amylopectin molecules are present in comparatively higher proportion as in the case of waxy starch, the branches prevent the degree of reformation of the hydrogen bonds and therefore, it results generally into a weak gel.



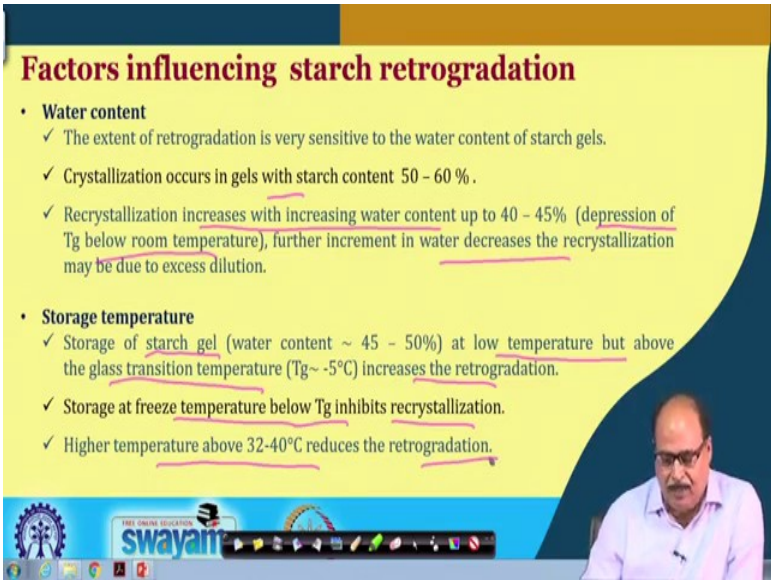
This is a schematic representation of the changes that occur in a starch-water mixture during heating, cooling and storage. In this 'I' represents the native starch granules when it is heated in water, the granules absorb water and it becomes swollen. When followed by further heating, it is continued to ‘II b’ where amylose leaching and partial granule disruption occurs which results in the pasting of the starch. Further, the formation of an ordered or crystalline amylose molecule during the cooling process can be observed and finally, there is formation of ordered or crystalline amylopectin molecules during storage. So, this is the way of structure formation of starch during cooling and storage. These changes ultimately affect the texture and other characteristics of the material e.g. rice - when the rice is cooked, after cooking when it is cooled down undisturbed; different types of texture in the cooked rice can be observed such as soft rice and hard rice depending upon the starches and the changes that have occurred during this process of cooking.



Retrogradation

Another important phenomenon is the retrogradation of starch in which the reassociation of the amylopectin or amylose molecule after the gelatinization can be observed during the cooling process.

Starch retrogradation refers to the reassociation or the recrystallization of the polysaccharide in gelatinized starch i.e. amylose and amylopectin. It occurs more rapidly with amylose than the amylopectin, since amylose is a smaller unbranched molecule. Retrogradation of starch is affected by storage temperature, composition such as water content, sugar, lipid, salt and anti-staling agents present in the system.



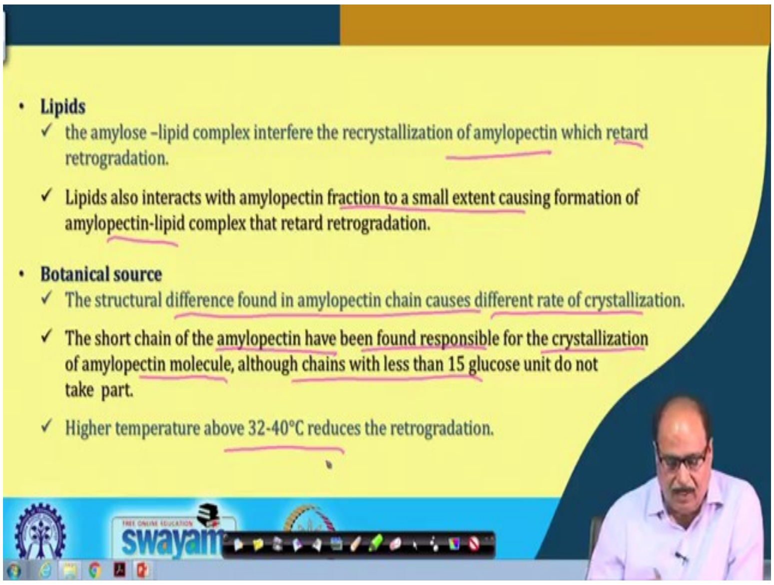
Factors influencing starch retrogradation

(i) Water content

The presence of water in the material affects the starch retrogradation process. The crystallization occurs in gel with a starch content of up to 50 to 60 %. Recrystallization increases with increasing water content up to 40 to 45 % which is the result of depression of the glass transition temperature (Tg) below room temperature. The further increment in water decreases the recrystallization and this may be due to excessive dilution.

(ii) Storage temperature

Similarly, storage of starch gel (water content ~ 45-50%) at a lower temperature, but above the glass transition temperature (Tg~-5°C) the retrogradation increases. Storage at freeze temperature below Tg inhibits recrystallization and higher temperature above 32 to 40 °C reduces the retrogradation phenomena.



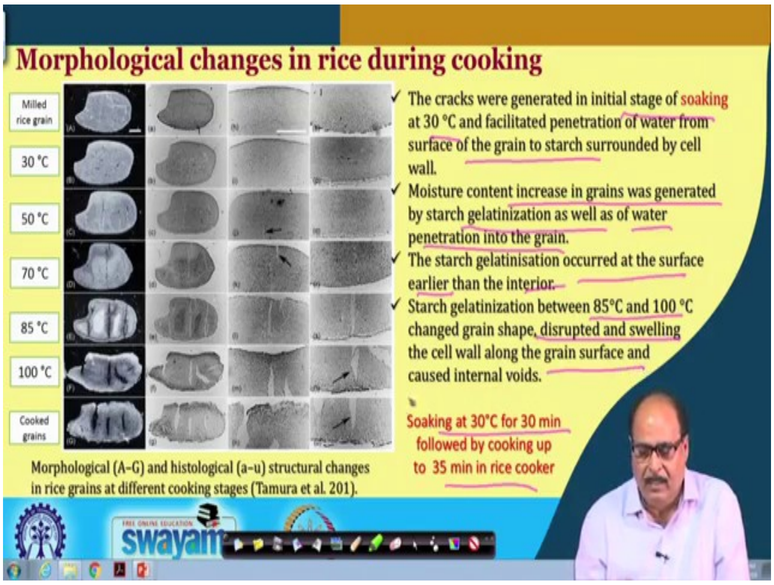
(iii) Lipids

Amylose-lipid complex interferes with the recrystallization process of amylopectin which retards retrogradation. Lipids also interact with amylopectin fraction to a small extent causing the formation of amylopectin lipid complex that retards the retrogradation process.

(iv) Botanical source

The structural difference found in the amylopectin chain of starches from the various sources also cause differences in the rate of crystallization processes.

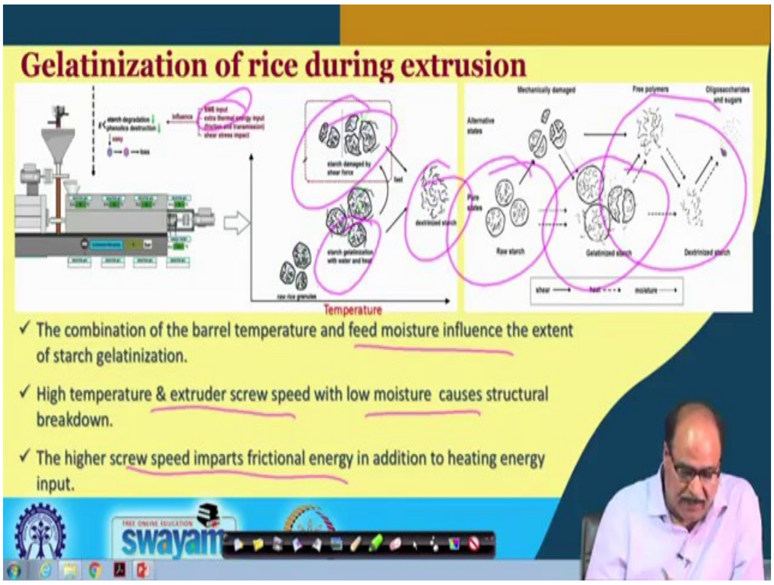
The short chain of the amylopectin has been found to be responsible for the crystallization of amylopectin molecule, although chains with less than 15 glucose units do not take part.



Morphological changes in rice during cooking

The figure shows morphological changes and histological structural changes in the rice grain when it is soaked for 30 min at 30 °C followed by cooking from 50 to 100 °C for 35 min in rice cookers. The cracks were generated in the initial stage of soaking at 30 °C and facilitated penetration of water from the surface of the grain to starch surrounded by a cell wall.

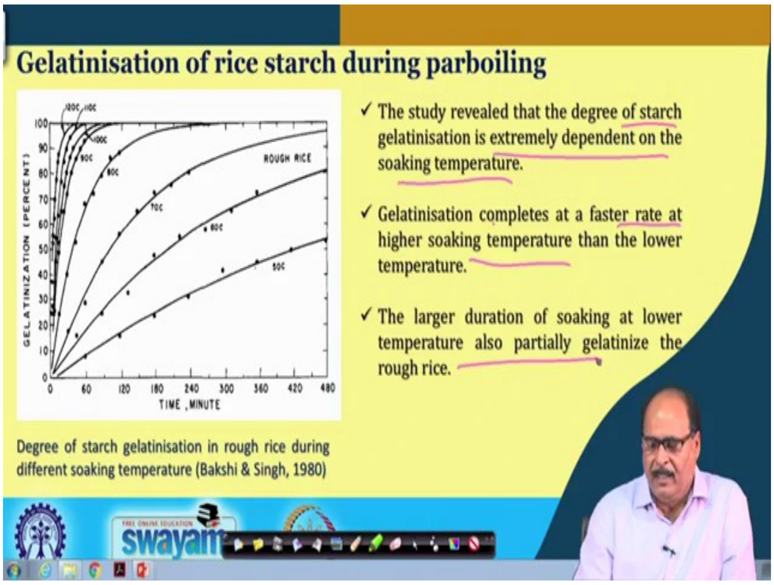
Moisture content increase in grains was generated by the starch gelatinization process as well as water penetration into the grain. The gelatinization occurred at the surface earlier than in the interior. The starch gelatinization between 85 and 100 °C changed the grain shape, resulted into the disruption and swelling of the cell wall along the grain surface and caused internal voids.



Gelatinization of rice during extrusion

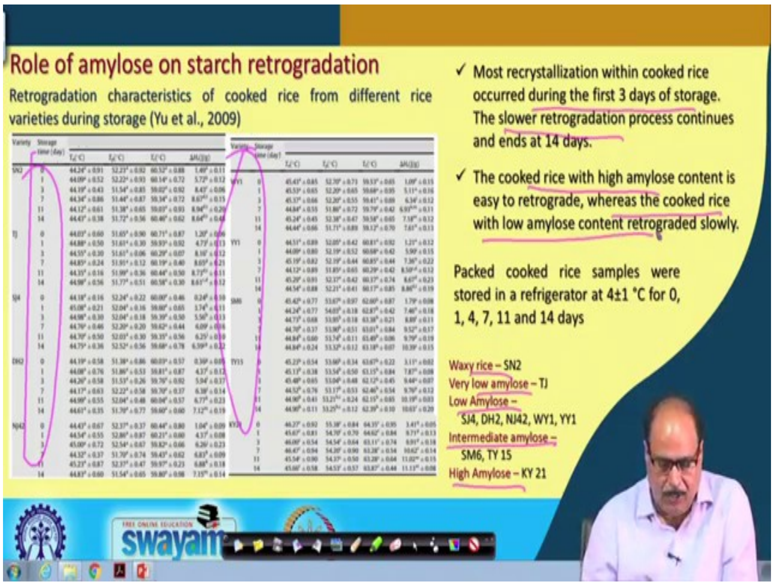
In this slide, the changes in the starch material i.e. gelatinization, fragmentation and dextrination during extrusion processes is shown. The combination of barrel temperature and specific mechanical energy input combined with feed moisture influences the starch gelatinization process during extrusion. High temperature and extruder screw speed with low moisture cause a structural breakdown and starch damage due to shear force, etc. The starch granules undergo the gelatinization process and then starch is finally, damaged and broken down into intermediate molecules i.e. the dextrins which have intermediate properties between glucose and starch.

The high screw speed imparts frictional energy in addition to heat energy input during extrusion of starch. This high shear, temperature and moisture gelatinize and break the starch into free polymers or even dextrinized starch or oligosaccharides and sugar.



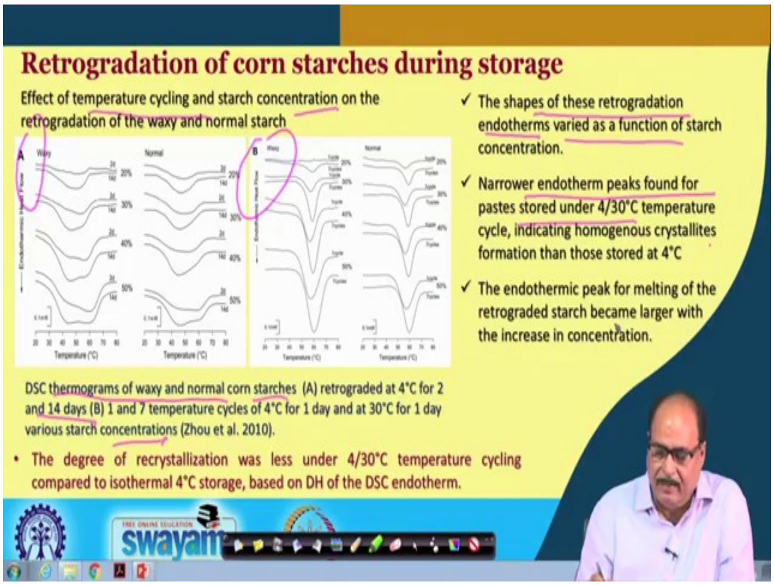
Gelatinization of rice starch during parboiling

During the parboiling process, it was reported in literature that the degree of starch gelatinization in rough rice during different soaking temperatures increases with increase in the time as well as temperature. The degree of starch gelatinization is extremely dependent on the soaking temperature as it completes at a faster rate at higher soaking temperature than at lower temperature. The larger duration of soaking at lower temperature also resulted in partial gelatinization of the rough rice.



Role of amylose on starch retrogradation

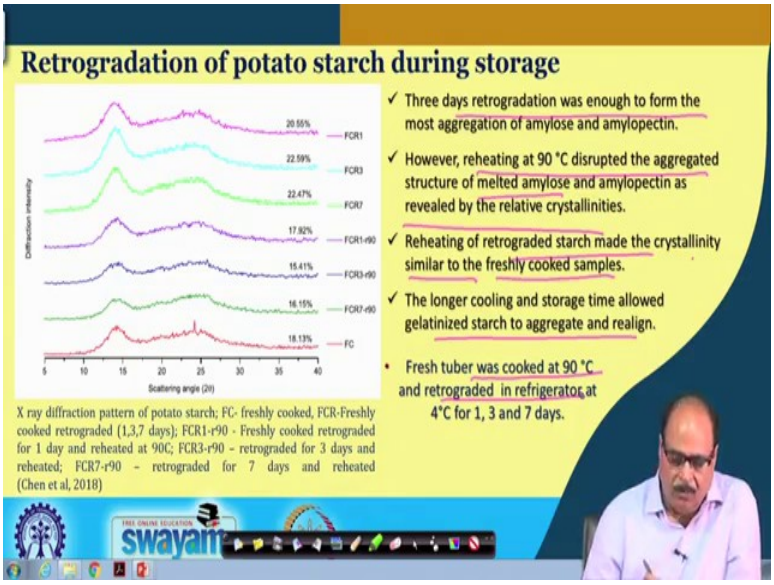
In this, a study conducted by Yu et al. is presented. They have shown the role of starch amylose and its effect on the retrogradation. Different rice varieties such as waxy rice, very low amylose-containing rice, low amylose-containing rice, intermediate amylose-containing rice and high amylose containing rice were studied. It was found that most recrystallization within cooked rice occurred during the first 3 days of storage and the slower retrogradation process continues and ends at 14 days of storage. The cooked rice with high amylose content is easy to retrograde whereas, the cooked rice with low amylose content retrograded slowly.



Retrogradation of corn starches during storage

Retrogradation of corn starch during storage can be seen in these figures. These are the DSC thermographs of waxy and normal corn starches (A) retrograded at 4 °C for 2 and 14 days whereas, (B) 1 and 7 temperature cycles of 4 °C for 1 day and 30 °C for 1 day at various starch concentrations.

The shapes of these retrogradation endotherms varied as a function of starch concentration. Narrower endotherm peak was found for the paste stored under 4 / 30 °C temperature cycle, indicating homogeneous crystallites formation than those stored at 4 °C. The endothermic peak for the melting of the retrograded starch became larger with the increase in concentration.



Retrogradation of potato starch during storage

There is another similar study showing the retrogradation of potato starch during storage. The experiment was conducted where these fresh potato tubers were cooked at 90 °C and retrograded in the refrigerator at 4 °C for 1, 3 and 7 days. The x-ray diffraction patterns of potato starch were studied. It was found that, 3 days retrogradation was enough to form the most aggregation of amylose and amylopectin. However, reheating at 90 °C disrupted the aggregated structure of melted amylose and amylopectin as revealed by the relative crystallinities. Reheating of retrograded starch made the crystallinity similar to the freshly cooked samples. The longer cooling and storage time allowed gelatinized starch to aggregate and realign.

So, these important processes viz. retrogradation and gelatinization influence the characteristics of the starch-containing materials and finally, affect to a great extent to their eating qualities or to their functionalities during food processing and preparation.