Consortium for
Educational
Communication

Module
on
Starch And Cellulose

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TEXT

1. INTRODUCTION:

Carbohydrates occur in plant and animal tissues as well as in microorganisms in many different forms and levels. In plants, a wide variety of monosaccharides and oligosaccharides occur, and the storage polysaccharide is starch. Starch is a mixture of two different polysaccharides built out of glucose, and forms a white, tasteless powder when purified. Cellulose is one of many polymers found in nature. Wood, paper, and cotton all contain cellulose. Cellulose is made of repeat units of the monomer glucose. Because cellulose is built out of a sugar monomer, it is called a polysaccharide. The following section discuss in detail about starch and cellulose.

2. STARCH:

2.1 Occurrence and Isolation:

Starch is widely distributed in various plant organs as a storage carbohydrate. As an ingredient of many foods, it is also the most important carbohydrate source in human nutrition. In addition, starch and its derivatives are important industrially, for example, in the paper and textile industries. Starch is isolated mainly from the sources such as corn, potato, rice, wheat, sweet potato, lotus root etc. Recently, starches obtained from legumes (peas, lentils) have become more interesting because they have properties which appear to make them a suitable substitute for chemically modified starches in a series of products. Starches of various origin have individual, characteristic properties which go back to the shape, size, size distribution, composition, and crystallinity of the granules. In some cases, e.g., potato tubers, starch granules occur free, deposited in cell vacuoles; hence, their isolation is relatively simple. The plant material is disintegrated, the starch granules are washed out with water, and then sedimented from

the "starch milk" suspension and dried. In other cases, such as cereals, the starch is embedded in the endosperm protein matrix; hence, granule isolation is a more demanding process. Thus, a counter-current process with water at 50◦C for 36–48 h is required to soften corn (steeping step of processing). The steeping water contains 0.2% SO_2 in order to loosen the protein matrix and, thereby, to accelerate the granule release and increase the starch yield. The corn grain is then disintegrated. The germ, due to its high oil content, has a low density and is readily separated by flotation. It is the source for corn oil isolation. The protein and starch are then separated in hydrocyclones. The separation is based on density difference (protein < starch). The protein by-product is marketed as animal feed or used for production of a protein hydrolysates (seasoning). The recovered starch is

washed and dried. In the case of wheat flour, a dough is made first, from which a raw starch suspension is washed out. After separation of fiber particles from this suspension, the starch is fractionated by centrifugation. In addition to the relatively pure primary starch, a finer grained secondary starch is obtained which contains pentosans. The starch is then dried and further classified. The residue, gluten serves as a raw material in the production of food seasoning and in the isolation of glutamic acid. If dried gently, it retains its baking quality and is used as a flour improver. In the case of rye, the isolation of starch is impeded by the relatively high content of swelling agents. Starch isolated from the tubers of various plants in tropical countries is available on the market under a variety of names (e.g., canna, maranta, and tacca starch).

2.2 **Structure and Properties:**

Starch comprises of two basic molecular components: amylose and amylopectin. These are identical in their constituent basic units (glucose), but differ in their structural organization (linkages). These variations in the linkages in turn affect their functionality in food applications. Amylose is a straight chain molecule, while amylopectin is a branched molecule. In addition, each is hydrolyzed, digested, and absorbed differently. Amylose is hydrolyzed mainly by amylases, while amylopectin requires debranching enzymes such as pullulanase for complete hydrolysis. As a result of their structure, the nature and products of hydrolysis of amylose and amylopectin differ. The proportions of amylose and amylopectin in foods therefore influence the extent of digestibility of the starch.

Amylose is a chain polymer of α-D-glucopyranosyl residues linked by 1→4 linkage (Fig1):

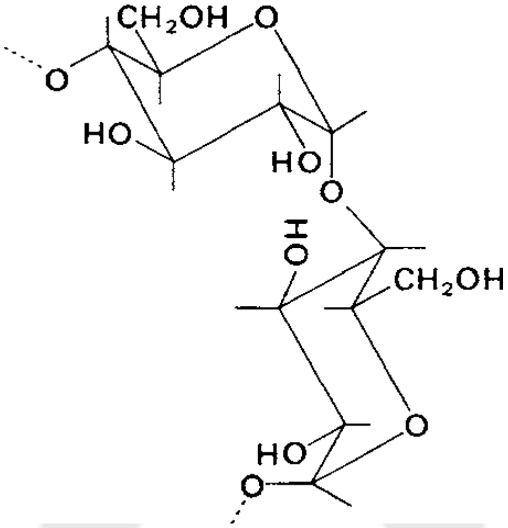

Fig. 1: Structure of Amylose

The molecular size of amylose is variable. The polymerization degree in wheat starch lies between 500 and 6000, while in potatoes it can rise up to 4500. This corresponds to a molecular weight of 150–750 kD. Amylose is the key component involved in water absorption, swelling, and gelation of starch in food processing. High amylose starches are therefore most commonly applied in food products that require quick-setting gels such as candies and confectionery. Amylose is more susceptible to gelatinization and retrogradation, and hence is most commonly involved in resistant starch formation.

Amylopectin (Fig 2) is a branched glucan with side chains attached in the 6-position of the glucose residues of the principal chain:

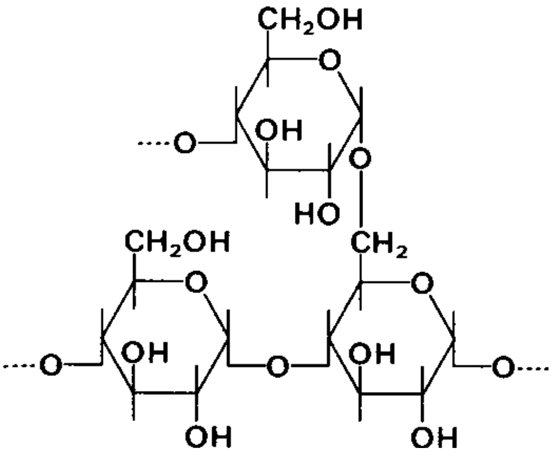

Fig. 2: Structure of amylopectin

An average of 20–60 glucose residues is present in short chain branches and each of these branch chains is joined by linkage of C-1 to C-6 of the next chain. The main portion of a starch granule's crystalline structure is apparently derived from amylopectin. The degree of polymerization of amylopectin (wheat) lies in the range of 3×10^5–3×10^6 glucose units, which corresponds to a molecular mass of 5×10^7–5×10^8 g/mol. One phosphoric acid residue is found for an average of 400 glucose residues.

The organization of amylopectin molecules in starch granules is shown in Fig. 3: it is radial, the reducing end being directed outwards.

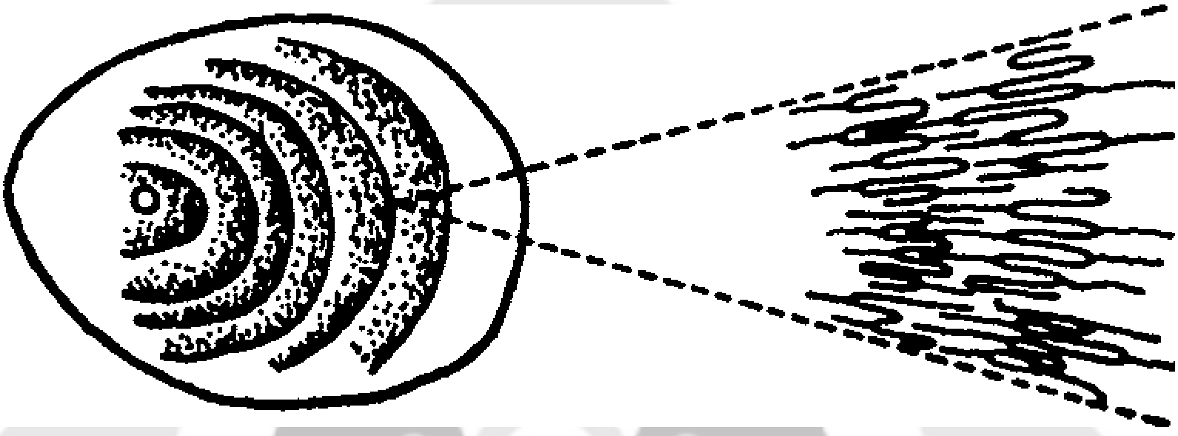

Fig. 3: Arrangement of amylopectin in starch granules

Amylopectin, when heated in water, forms a transparent, highly viscous solution, which is ropy, sticky, and coherent. Unlike with amylose, there is no tendency toward retrogradation. There are no staling or aging phenomena and no gelling, except at very high concentrations. High amylopectin starches (waxy starches) are therefore commonly used in noodle processing and in some baked products to extend shelf-life. However, there is a rapid viscosity drop in acidic media and on autoclaving or applying stronger mechanical shear force.

2.3 Utilization:

Starch is an important thickening and binding agent and is used extensively in the production of puddings, soups, sauces, salad dressings, diet food preparations for infants, pastry filling, mayonnaise, etc. Corn starch is the main food starch and an important raw material for the isolation of glucose. A layer of amylose can be used as a protecting cover for fruits (dates or figs) and dehydrated and candied fruits, preventing their sticking together. Amylose treatment of French fries decreases their susceptibility to oxidation. The good gelling property of a dispersable amylose makes it a suitable ingredient in instant puddings or sauces. Amylose films can be used for food packaging, as edible wrapping or tubing, as exemplified by a variety of instant coffee or tea products. Amylopectin utilization is also diversified. It is used to a large extent as a thickener or stabilizer and as an adhesive or binding agent.

2.4 Starch types:

2.4.1 Resistant Starch

Starch and its degradation products which are not absorbed in the small intestine are called resistant starch (RS). RS can, however, be metabolized by the bacteria of the colon. Acetic acid, propionic acid and butyric acid are formed, stimulating the growth of the cells of the intestinal epithelium. Especially butyric acid has been found to positively affect health. A distinction is made between 4 forms of RS: Type I, starch enclosed in cells

(e. g., coarse-ground grain or legumes), Type II, native starch granules (e. g., in bananas, potatoes), Type III, starch fractions produced on retrogradation (e. g., in boiled potatoes, bread crumb), and Type IV, starch modified by the *Maillard* reaction or caramelization (formation of glycosidic bonds which are not hydrolyzed by α-amylase).

2.4.2 Modified Starches

The properties of Starch and its components can be improved or “tailored” by physical and chemical methods to fit or adjust the properties

to a particular application or food product. Such starches are known as modified starches and include:

2.4.2.1 Mechanically Damaged Starches

When starch granules are damaged by grinding or by application of pressure at various water contents, the amorphous portion is increased, resulting in improved dispersibility and swellability in cold water, a decrease in the gelatinization temperature by 5–10 ◦C, and an increase in enzymatic

vulnerability. In bread dough made from flour containing damaged starch, for instance, the uptake of water is faster and higher and amylose degradation greater.

2.4.2.2 Dextrins

Heating of starch (<15% of water) to 100–200◦C with small amounts of acidic or basic catalysts causes more or less extensive degradation. White

and yellow powders are obtained which deliver clear or turbid, highly sticky solutions of varying viscosity. These products are used as adhesives in

sweets and as fat substitutes.

2.4.2.3 Pregelatinized Starch

Heating of starch suspensions, followed by drying, provides products that are swellable in cold water and form pastes or gels on heating. These products are used in instant foods, e.g., pudding, and as baking aids.

2.4.2.4 Oxidized Starches

Starch hydrolysis and oxidation occur when aqueous starch suspensions are treated with sodium hypochlorite at a temperature below the starch gelatinization temperature range. The products obtained have an average of one carboxyl group per 25–50 glucose residues. Oxidized starch is used as lower-viscosity filler for salad dressings and mayonnaise. Unlike thin boiling starch, oxidized starch does not retrograde nor does it set to an opaque gel.

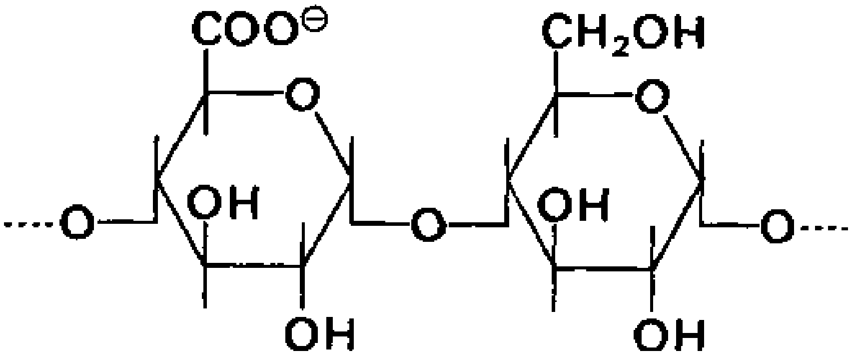

Fig. 4: Structure of oxidized starch

2.5 Gelatinization and Retrogradation:

When suspended in cold water, air-dried starch granules swell with an increase in diameter of 30–40%, the process being referred to as gelatinization. If this suspension is heated, irreversible changes occur starting at a certain temperature, which is characteristic of each type of starch (50–70°C), called the gelatinization temperature. The starch granules absorb 20–40 g of water/g of starch, the viscosity of the suspension rising steeply. At the same time, a part of the amylose diffuses out of the granule and goes into solution. Finally, the granule bursts. In gelatinization, water first diffuses into the granule, crystalline regions then melt with the help of hydration, and, finally, swelling gives rise to a solution through further diffusion of water. In this process, hydrogen bridges between glucose chains in the crystallites are primarily disrupted and perhaps some of those in the amorphous regions as well. It is probable that the swelling of the amorphous regions facilitates the dissolving out of amylose from the crystallites, which are thereby destabilized. Dried starch with 1–3% of water undergoes only slight changes up to a temperature of 180°C, whereas starch with 60% of water completely gelatinizes at temperatures as low as 70°C. Dried starch with 1–3% of water undergoes only slight changes up to a temperature of 180°C, whereas starch with 60% of water completely gelatinizes at temperatures as low as 70°C.

Cooling of gelatinized starch results in the re-association of the leached amylose from gelatinized granules. This is the process of retrogradation. This term denotes the largely irreversible transition from the solubilized or highly swollen state to an insoluble, shrunken, microcrystalline state. This state can also be directly achieved by slowly cooling a starch paste. The tendency towards retrogradation is enhanced at low temperatures, especially near 0°C, neutral pH values, high concentration, and by the absence of surface active agents. It also depends on the molecular weight and on the type of starch, e.g., it increases in the series potato < corn < wheat. The transitions described from very water-deficient starting states via very highly swollen states or solutions to more or less shrunken states are linked to changes in the interactions between the glucans and to conformational changes. Retrogradation is also referred to as setback, and occurs with re-crystallization of amylose. Amylose is much more susceptible to retrogradation and amylopectin is only minimally involved in starch retrogradation even though amylopectin has been shown to influence retrogradation and syneresis in corn starch gels. This re-association and re-crystallization of amylose causes release of the water absorbed and bound during gelatinization, leading to the phenomenon known as syneresis.

Retrogradation of starch in food products is a concern as it affects product quality. The stability of starch-containing products during cold storage in particular is greatly affected by the extent of retrogradation. Freeze-thaw cycles result in extensive retrogradation and syneresis. Retrogradation of starch in some instances enhances quality as such starches are resistant to enzyme hydrolysis.

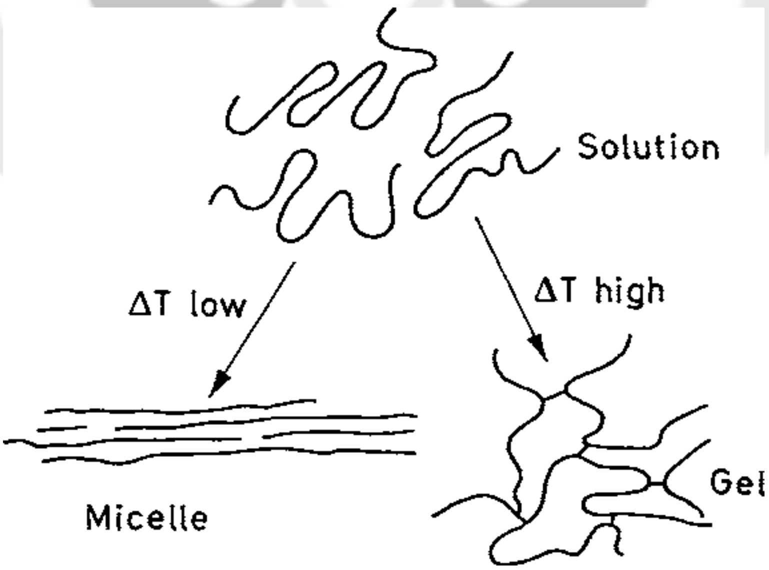

Fig. 5: Behavior of amylose molecules during cooling of a concentrated aqueous solution

3. CELLULOSE:

3.1 Occurrence and Isolation:

Cellulose is the main constituent of plant cell walls, where it usually occurs together with hemicelluloses, pectin and lignin. Since cellulase enzymes are absent in the human digestive tract, cellulose, together with some other inert polysaccharides, constitute the indigestible carbohydrate of plant food (vegetables, fruits or cereals), referred to as dietary fiber. Cellulases are also absent in the digestive tract of animals, but herbivorous animals can utilize cellulose because of the rumen microflora (which hydrolyze the cellulose). The importance of dietary fiber in human nutrition appears mostly to be the maintenance of intestinal motility (peristalsis).

3.2 Structure and Properties:

Cellulose (Fig 6) consists of β-glucopyranosyl residues joined by 1→4 linkages.

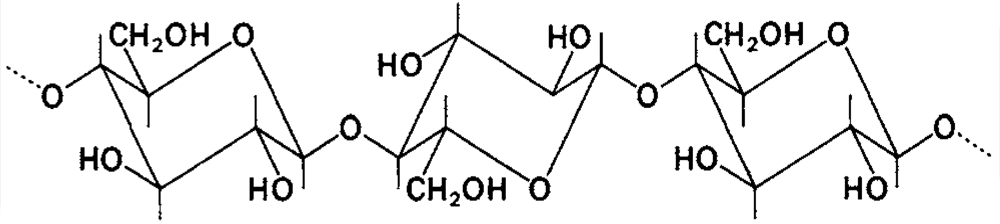

Fig. 6: structure of cellulose

Cellulose crystallizes as monoclinic, rod-like crystals. The chains are oriented parallel to the fiber direction and form the long b-axis of the unit cell. The crystalline sections of cellulose comprise an average of 60% of native cellulose. These sections are interrupted by amorphous gel regions, which can become crystalline when moisture is removed. The acid- or alkali-labile bonds also apparently occur in these regions. Microcrystalline cellulose is formed when these bonds are hydrolyzed. This partially depolymerized cellulose product with a molecular weight of 30–50 kdal, is still water insoluble, but does not have a fibrose structure.

Cellulose has a variable degree of polymerization (denoted as DP; number of glucose residues per chain) depending on its origin. The DP can range from 1000 to 14,000 (with corresponding molecular weights of 162 to 2268 kdal). Because of its high molecular weight and crystalline structure, cellulose is insoluble in water. In addition, its swelling power or ability to absorb water, which depends partly on the cellulose source, is poor or negligible.

3.3 Utilization:

Microcrystalline cellulose is used in low-calorie food products and in salad dressings, desserts and ice creams. Its hydration capacity and dispersibility are substantially enhanced by adding it in combination with small amounts of carboxymethyl cellulose.

3.4 Cellulose Derivatives:

Cellulose can be alkylated into a number of derivatives with good swelling properties and improved solubility. Such derivatives have a wide field of application.

3.4.1 Alkyl cellulose, Hydroxyalkyl cellulose

The reaction of cellulose with methylchloride or propylene oxide in the presence of a strong alkali introduces methyl or hydroxypropyl groups into cellulose leading to its alkylation (Fig 7).

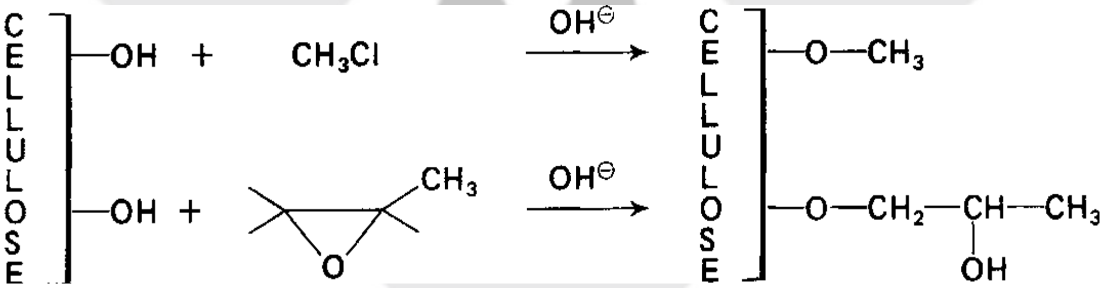

Fig. 7: Alkylation of cellulose

The degree of substitution (DS) is dependent on reaction conditions.

Mixed substituted products are also produced, e.g., methylhydroxypropyl cellulose or methylethyl cellulose. The substituents interfere with the normal crystalline packing of the cellulose chains, thus facilitating chain solvation. Depending on the nature of the substituent (methyl, ethyl, hydroxymethyl, hydroxyethyl or hydroxypropyl) and the substitution degree, products are obtained with variable swelling powers and water solubilities. A characteristic property for methyl cellulose and double-derivatized methylhydroxypropyl cellulose is their initial viscosity drop with rising temperature, setting to a gel at a specific temperature. Gel setting is reversible. Gelling temperature is dependent on substitution type and degree.

Hydroxyalkyl substituents stabilize the hydration layer around the macromolecule and, thereby, increase the gelling temperature. Changing the proportion of methyl to hydroxypropyl substituents can vary the gelling

temperature within a wide range. The above properties of cellulose derivatives permit their diversified applications. In baked products obtained from gluten-poor or gluten-free flours, such as those of rice, corn or rye, the presence of methyl and methylhydroxypropyl celluloses decreases the crumbliness and friability of the product, enables a larger volume of water to be worked into the dough and, thus, improves the extent of starch swelling during oven baking. Since differently substituted celluloses offer a large choice of gelling temperatures, each application can be met by using the most suitable derivative. Their addition to batter or a coating mix for meats decreases oil uptake in frying. Their addition to dehydrated fruits and vegetables improves rehydration characteristics and texture upon reconstitution. Sensitive foods can be preserved by applying alkyl cellulose as a protective coating or film. Cellulose derivatives can also be used as thickening agents in low calorie diet foods. Hydroxypropyl cellulose is a powerful emulsion stabilizer, while methylethyl cellulose has the property of a whipping cream: it can be whipped into a stable foam consistency.

3.4.2 Carboxymethyl Cellulose

Carboxymethyl cellulose is obtained by treating alkaline cellulose with chloroacetic acid. The properties of the product depend on the degree of substitution (DS; 0.3–0.9) and of polymerization (DP; 500–2000). Low substitution types (DS ≤0.3) are insoluble in water but soluble in alkali, whereas higher DS types (>0.4) are water soluble. Solubility and viscosity are dependent on pH. Carboxymethyl cellulose is an inert binding and thickening agent used to adjust or improve the texture of many food products, such as jellies, paste fillings, spreadable process cheeses, salad dressings and cake fillings and icings. It retards ice crystal formation in ice cream, stabilizing the smooth and soft texture. It retards undesired saccharose crystallization in candy manufacturing and inhibits starch retrogradation or the undesired staling in baked goods. Lastly, Carboxymethyl cellulose improves the stability and rehydration characteristics of many dehydrated food products.